NAVAL FACILITIES ENGINEERING COMMAND
Washington, DC 20374-5065

NAVFAC

NFESC
Contract Report
CR 00-005-ENV

ENHANCED IN SITU ANAEROBIC BIOREMEDIATION OF FUEL-CONTAMINATED GROUND WATER

by

Dr. Martin Reinhard, Mr. Gary Hopkins,
and Dr. Jeff Cunningham
Department of Civil and Environmental Engineering
Stanford University

and

Carmen A. Lebron
Restoration Development Branch
Naval Facilities Engineering Service Center

September 2000

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 2000	Final; Oct 1995 – Dec 1999

4. TITLE AND SUBTITLE

ENHANCED IN SITU ANAEROBIC BIOREMEDIATION OF FUEL-CONTAMINATED GROUND WATER

5. FUNDING NUMBERS

6. AUTHOR(S)

Dr. Martin Reinhard, Gary Hopkins, Dr. Jeff A. Cunningham, and Carmen Lebron

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Stanford University
Department of Civil and Environmental Engineering
Stanford, CA 94305-4020

8. PERFORMING ORGANIZATION REPORT NUMBER

CR 00-005-ENV

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Environmental Security Technology Certification Program
901 North Stuart Street, Suite 303
Arlington, VA 22203

10. SPONSORING/MONITORING AGENCY

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Enhanced anaerobic biodegradation of ground water contaminated by fuel hydrocarbons has been evaluated at a field demonstration conducted at the Naval Weapons Station, Seal Beach, California. This demonstration included establishing three different remediation zones in situ: one zone was augmented with sulfate, one was augmented with sulfate and nitrate, and the third was not augmented. This enables a comparison of hydrocarbon biodegradation under sulfate-reducing, sequential denitrifying/sulfate-reducing, and methanogenic conditions, respectively. In general, the results from the field demonstration are: (1) Certain fuel hydrocarbons were removed preferentially over others, but the order of preference depends on the geochemical conditions; and (2) in the zones that were augmented with sulfate and/or nitrate, the added electron acceptors were consumed quickly, indicating that enhancement via electron acceptor injection accelerates the biodegradation process. More specifically, in the sulfate-reducing zone, sulfate was utilized with an apparent first-order rate coefficient of approximately 0.1/day. In the combined denitrifying/sulfate-reducing zone, nitrate was utilized preferentially over sulfate, with an apparent first-order rate coefficient of 0.1-0.6/day. With regard to the aromatic BTEX hydrocarbons, toluene was preferentially removed under intrinsic conditions; biodegradation of benzene was slow if it occurred at all; augmentation with sulfate preferentially stimulated biodegradation of o-xylene; and ethylbenzene appeared recalcitrant under sulfate-reducing conditions but readily degradable under denitrifying conditions.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Anaerobic bioremediation, BTEX degradation, nitrate reducing conditions, fuel bioremediation	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
U	U	U	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

EXECUTIVE SUMMARY

Enhanced anaerobic biodegradation of groundwater contaminated by fuel hydrocarbons has been evaluated at a field demonstration conducted at the Naval Weapons Station, Seal Beach, California. This demonstration included establishing three different remediation zones in situ: one zone was augmented with sulfate, one was augmented with sulfate and nitrate, and the third was not augmented. This enables a comparison of hydrocarbon biodegradation under sulfate-reducing, sequential denitrifying/sulfate-reducing, and methanogenic conditions, respectively. The results from the field demonstration are: (1) Certain fuel hydrocarbons were removed preferentially over others, but the order of preference depends on the geochemical conditions; and (2) in the zones that were augmented with sulfate and/or nitrate, the added electron acceptors were consumed quickly, indicating that enhancement via electron acceptor injection accelerates the biodegradation process. More specifically, in the sulfate-reducing zone, sulfate was utilized with an apparent first-order rate coefficient of approximately 0.1/day. In the combined denitrifying/sulfate-reducing zone, nitrate was utilized preferentially over sulfate, with an apparent first-order rate coefficient of 0.1-0.6/day. With regard to the aromatic BTEX hydrocarbons, toluene was preferentially removed under intrinsic conditions; biodegradation of benzene was slow if it occurred at all; augmentation with sulfate preferentially stimulated biodegradation of o-xylene; and ethylbenzene appeared recalcitrant under sulfate-reducing conditions but readily degradable under denitrifying conditions.

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1. Introduction

1.1 Background Information

Ground water contamination is a significant problem at thousands of Department of Defense (DOD) installations and formerly used defense sites. Particularly common is ground water contamination from fuel hydrocarbons, which often leak from underground storage tanks. The primary contaminants of concern in fuel hydrocarbon spills are benzene, toluene, ethylbenzene, and xylene, collectively known as BTEX. Benzene is a known human carcinogen with a drinking water maximum contaminant level (MCL) of 5 parts per billion (ppb). Toluene, ethylbenzene, and xylene have MCLs of 1 part per million (ppm), 0.7 ppm, and 10 ppm, respectively; exposure above these levels might impair human health. Therefore, the widespread contamination from BTEX represents a significant environmental problem, both at DoD sites and at privately owned properties throughout the United States.

The commonly used pump-and-treat method for removing contamination from ground water has proven to be much more expensive, time consuming, and inefficient than first envisioned. As a result, in situ bioremediation is now being investigated, evaluated, and, in some cases, applied as a remediation technology at contaminated ground water sites. The principle of in situ bioremediation is that certain bacteria, found naturally in ground water aquifers, can metabolize particular contaminants, thereby reducing the contaminant concentrations without extracting the water from the aquifer. These metabolic processes, coupled with other naturally occurring processes that can reduce the contaminant concentrations in ground water, are referred to as natural attenuation. When naturally occurring metabolic processes are used to remediate a contaminated site without any additional alteration of site conditions, the process is referred to as intrinsic in situ bioremediation. When conditions at the site are engineered or altered in order to stimulate or accelerate the biological destruction of contaminants, the process is referred to as enhanced in situ bioremediation. The United States Environmental Protection Agency (EPA) has recently outlined its policy on the use of monitored natural attenuation (i.e., intrinsic bioremediation, with appropriate monitoring) for the remediation of contaminated soil and ground water at sites regulated under Office of Solid Waste and Emergency Response programs [U.S. EPA, 1997b].

In the case of contamination by fuel hydrocarbons, it is now well known that many microorganisms indigenous to soil can oxidize (mineralize) the contaminants to harmless carbon dioxide and water. This process can occur rapidly under aerobic conditions, i.e., in the presence of oxygen. Under anaerobic conditions (in the absence of oxygen), the process can still occur, but is not as well understood. Nitrate, sulfate, ferric iron, or carbon dioxide can replace oxygen as the terminal electron acceptor (oxidant). Because of its relative simplicity and low cost, intrinsic bioremediation is often the method of choice for remediating fuel hydrocarbons [U.S. EPA, 1997b]. However, intrinsic bioremediation can be slow, is often unpredictable, and may be inadequate for many sites, particularly under anaerobic conditions. Thus, engineered intervention (enhancement) might be necessary in order for the oxidation to proceed at acceptable rates.

Enhanced bioremediation might consist of augmenting the contaminated zone with electron acceptor(s), removing products that inhibit the oxidation reaction, or both.

The potential benefits from this technology are large. The principal advantage of bioremediation over conventional pump-and-treat remediation is that the contaminants are destroyed in situ and no secondary waste streams are produced needing further treatment. In situ bioremediation might be susceptible to some of the same impediments that limit the efficiency of the pump-and-treat method; for example, slow contaminant leaching of adsorbed contaminants from aquifer solids can present a continuing source of contamination. However, maintaining the presence of electron acceptors in the contaminated aquifer via periodic injection should be far less expensive than continuous ground water extraction. Therefore, for sites where it can be shown that enhanced in situ bioremediation is technically feasible, it should be less expensive to implement than a pump-and-treat system.

This report describes the results of a project that was intended to meet two aims:

(1) Demonstration of a technology by which contaminants (principally BTEX) are removed from ground water via enhanced in situ anaerobic biodegradation
(2) Investigation of the factors that govern anaerobic biodegradation of fuel hydrocarbons (principally BTEX) under three different types of geochemical conditions.

In order to achieve both of these goals, a system of injection and extraction wells was installed at a fuel-contaminated site. Because one of the goals of this project was quantification of the efficacy of anaerobic bioremediation under particular geochemical conditions, the system was equipped with more observation points and greater operational controls than necessary for a typical application. Throughout the remainder of this report, we note the particular aspects in which our operation differed from the recommended operation at other contaminated sites. Here we also note that this project was not intended to address the removal of methyl *tert*-butyl ether (MTBE), a gasoline additive that is commonly found in ground water at sites contaminated with BTEX.

1.2 Official Department of Defense (DOD) Requirement Statement

The work accomplished under this effort responds to the following DOD environmental technology requirements:

Army: A (1.2.b), Enhanced Alternative and In-Situ Treatment Technologies for Organics (Non-Halogenated) in Groundwater (96–97)

Navy: (1.I.1.e), Improved remediation of groundwater contaminated with non-chlorinated hydrocarbons.

1.3 Objectives of the Demonstration

This project was intended to meet two broad objectives:

(1) Demonstration of a technology by which fuel hydrocarbons are removed from ground water via enhanced in situ anaerobic biodegradation
(2) Evaluation and quantification of the efficacy of three different anaerobic processes.

The focus of the technology demonstration was on the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene (BTEX). Previous laboratory and pilot-scale research had shown that BTEX compounds, especially toluene, can be mineralized under anaerobic conditions using nitrate or sulfate as an electron acceptor [Haag et al., 1991; Edwards et al., 1992; Ball and Reinhard, 1996; Reinhard et al., 1997]. This demonstration involved application of the previous results to a large field site. The site chosen for the demonstration was a contaminated portion of an aquifer at the Naval Weapons Station, Seal Beach, in southern California (Figures 1 and 2). This site was contaminated with fuel hydrocarbons from a leaking underground storage tank, as described in the report "Delineation of a hydrocarbon (weathered gasoline) plume in shallow deposits at the U.S. Naval Weapons Station, Seal Beach, California" [Schroeder, 1991].

With respect to objective (1), the technology demonstration, there were two specific goals:

(i) Validation of the technical viability of enhanced in situ anaerobic bioremediation, i.e., demonstration that anaerobic microbial processes can potentially be used for clean-up of sites contaminated with gasoline and/or other fuel hydrocarbons
(ii) Development of cost data for implementing the technology.

With respect to objective (2), the evaluation of anaerobic in situ bioremediation under different geochemical conditions, three different treatment zones (denitrifying, denitrifying and sulfate-reducing, and methanogenic) were established at the contaminated site. These zones are described in more detail in section 2.1.2, below.

The information developed in this project should allow responsible parties, consultants, remediation contractors, and the general public to better evaluate enhanced anaerobic in situ bioremediation as an option for treating sites contaminated with fuel hydrocarbons, and should contribute to the regulatory acceptance of this technology.

1.4 Regulatory Issues

There are three main regulatory issues with regard to the implementation of the technology described in this report:

(1) Nitrate, which has a drinking water maximum contaminant level (MCL) of 45 mg/L, is injected into the ground water as an electron acceptor. In order for the technology to operate at maximum efficiency, nitrate should be injected at a concentration higher than its MCL. Although nitrate is consumed rapidly after its injection, and therefore does not

represent a significant contamination risk, regulatory approval is required for injection of nitrate at high concentrations.

(2) Contaminated ground water is extracted, treated, augmented with electron acceptors, and then re-injected into the aquifer. The re-injection of treated ground water requires regulatory approval.

(3) It must be satisfactorily demonstrated that sufficient hydraulic control is established, so that the plume can be contained if any problem arises during implementation of the remediation technology.

Regulatory concern about these three issues is likely to vary from state to state and from region to region. Some methods for working with regulators to gain regulatory acceptance of this technology include the following.

(1) Using contaminated soil and water from the site in question, develop a laboratory microcosm experiment from which the utilization rate of nitrate can be estimated. The laboratory-derived utilization rate may differ from the actual utilization rate in a full-scale implementation, but the demonstration of rapid nitrate utilization would likely help to gain regulatory acceptance.

(2) Before re-injecting treated water into the aquifer, run the system in a pump-and-treat mode only, in order to demonstrate that the water treatment system is capable of removing contaminants of concern. This will provide regulators with the opportunity to evaluate the quality of the treated water that is to be re-injected.

(3) Before injection of electron acceptors (nitrate in particular), inject a tracer such as bromide, and then run the system in a pump-and-treat mode only, in order to demonstrate that the bromide can be fully recovered. This will provide regulators with the opportunity to evaluate the hydraulic control at the contaminated site.

(4) When nitrate is first injected, it should be injected at concentrations below its MCL of 45 mg/L -- perhaps about 15 mg/L. The next injection of nitrate can be at a higher concentration, but still below the MCL. That will give the microbial population a chance to adapt to the presence of nitrate, and will provide regulators with the opportunity to evaluate nitrate utilization in situ. If nitrate is consumed rapidly at concentrations below the MCL, regulators will be more likely to allow injection at concentrations which exceed the MCL.

1.5 Previous Testing of the Technology

Despite an abundance of laboratory data suggesting the probable success of enhanced in situ bioremediation, there have been relatively few field-scale demonstrations. In a few instances, technologies similar to the one described in this report have been tested elsewhere. Generally, the comparable technologies have been implemented in the following manner: water containing an electron acceptor (nitrate) is ponded in ditches, applied to the ground surface via sprinkler, or injected via wells into the vadose zone above a contaminated area. The water then infiltrates vertically into the contaminated zone, where the electron acceptor can stimulate biological transformation of BTEX. An extraction well is placed downgradient of the infiltration area to

collect any migrating contaminants that are not biodegraded. This technology has been applied at:

(1) U.S. Coast Guard station where JP-4 jet fuel was spilled [Hutchins, et al., 1991]
(2) Abandoned refinery [Battermann and Meier-Lohr, 1995]
(3) Pipeline spill in Park City, Kansas [Hutchins, et al., 1995]
(4) U.S. Air Force base where JP-4 jet fuel leaked from underground piping [Thomas, et al., 1995; Sweed, et al., 1996; Wiesner, et al., 1996]
(5) Military storage facility for jet fuel [Vroblesky, et al., 1997].

Many of these cases have reported partial or complete removal of BTEX compounds from the contaminated area. However, in these instances, it is not clear how much of the BTEX removal was due to anaerobic degradation, and how much was due to other processes such as aerobic degradation or extraction in the downgradient well. Furthermore, these studies were performed with augmentation of only a single electron acceptor, namely nitrate. One of the objectives of the demonstration described in this report is to investigate anaerobic bioremediation of BTEX with nitrate and sulfate as electron acceptors, and to evaluate nitrate- and sulfate-reducing conditions vis-a-vis methanogenic conditions. These different geochemical conditions are explained further in Section 2.1.1, below.

In another relevant field-scale study performed in the Borden aquifer in Ontario, Canada [Barbaro et al., 1992], it was found that toluene, ethylbenzene, and xylene could be partially degraded when the aquifer was enhanced with nitrate as an electron acceptor. In the absence of nitrate, contaminant degradation was considerably slower. Regardless of the nitrate concentration, benzene was recalcitrant, exhibiting very little transformation if any at all.

In general, studies have produced conflicting results regarding the likelihood for benzene removal via anaerobic biodegradation. Although benzene has sometimes been found to degrade under sulfate-reducing conditions [Edwards and Grbic-Galic, 1992; Lovley et al., 1995], nitrate-reducing conditions [Burland and Edwards, 1999], and methanogenic conditions [Grbic-Galic and Vogel, 1987], the degradation process appears to be very sensitive to experimental conditions. In other cases, benzene has been found recalcitrant under nitrate-reducing conditions [Acton and Barker, 1992; Ball and Reinhard, 1996; Reinhard et al., 1997] and under sulfate-reducing conditions [Edwards et al., 1992; Thierrin et al., 1995]. Therefore, one particularly interesting aspect of the project described in this report is the opportunity to evaluate benzene degradation under different anaerobic conditions (described below) at an actual field site.

2. Technology Description

2.1. Description

One of the two primary objectives of this project is to demonstrate a technology by which BTEX compounds are removed from ground water via enhanced in situ anaerobic biodegradation. This technology requires that we perform the following tasks:

(1) Determine the capacity of anaerobic bacteria for mineralizing fuel hydrocarbons under in situ conditions
(2) Establish a procedure for supplying electron acceptors to an aquifer contaminated with fuel hydrocarbons
(3) Establish a procedure for removing metabolic products that inhibit or interfere with the bioremediation process. In this regard, sulfide is probably of the greatest concern, because sulfate reduction is an important process in this technology, and anaerobic BTEX oxidation is known to be inhibited by high sulfide concentrations [Beller and Reinhard, 1995].

Sub-section 2.1.1, below, describes some of the fundamentals of the microbial degradation processes utilized in this demonstration. Sub-section 2.1.2 describes the engineering process utilized.

2.1.1 Microbial Degradation: Microorganisms are able to use BTEX contaminants as substrates for energy and growth, and electron acceptors such as oxygen, nitrate, or sulfate to convert the contaminants into harmless products (principally carbon dioxide and water), cell mass, and inorganic salts. In almost all cases, oxygen is consumed preferentially over alternate electron acceptors like sulfate or nitrate; after oxygen is consumed, anaerobic microorganisms use a series of alternate electron acceptors. With nitrate as the electron acceptor, nitrogen gas will be produced; with sulfate as the electron acceptor, hydrogen sulfide will be produced. Under methanogenic/ fermentative conditions, methane gas will be produced. In designing an enhanced anaerobic bioremediation system, the formation of these products must be considered.

Factors affecting the rate of BTEX biodegradation include:

(1) Abundance and nutritional status of the organisms
(2) Type and quantity of electron acceptors present
(3) Catabolic inhibition
(4) Toxicity
(5) Temperature

These factors are often difficult to quantify. The most commonly occurring alternate electron acceptors other than oxygen include nitrate, sulfate, ferric iron, and carbon dioxide. The stoichiometry of BTEX oxidation is considered below for aerobic, nitrate-reducing, sulfate-

reducing, and fermentative/methanogenic conditions, using toluene as a representative BTEX compound.

The aerobic biological degradation of toluene, ignoring cell growth, can be expressed as

$$C_7H_8 + 9\,O_2 \rightarrow 7\,CO_2 + 4\,H_2O \quad (1)$$

In this equation, toluene is completely mineralized to carbon dioxide and water, and the formation of biomass is not considered. This stoichiometry shows that the biodegradation of 1 mg/L toluene requires the presence of 3.1 mg/L dissolved oxygen in the ground water. When water and air are in equilibrium at 20°C, oxygen has a solubility of about 9 mg/L in water, which can degrade about 2.9 mg/L toluene. If toluene is present at higher concentrations, its aerobic degradation might be limited by the rate at which oxygen can be supplied to the contaminated zone. Liquid oxygen or hydrogen peroxide can be used to provide oxygen at concentrations higher than 9 mg/L, but these chemicals are expensive; also, as the system re-equilibrates to a dissolved oxygen concentration of 9 mg/L, oxygen bubbles will form in the aquifer, potentially causing hydraulic problems. Therefore, although aerobic BTEX degradation is a relatively rapid process, its rate can be limited by a low supply of oxygen.

Under nitrate-reducing (denitrifying) conditions, the stoichiometry for complete biodegradation of toluene to carbon dioxide is

$$C_7H_8 + 7.2\,H^+ + 7.2\,NO_3^- \rightarrow 3.6\,N_2 + 7.6\,H_2O + 7\,CO_2 \quad (2)$$

where cell growth has again been ignored. According to this stoichiometry, the biodegradation of 1 mg/L toluene requires the presence of 4.8 mg/L nitrate, i.e., more nitrate than oxygen is required to oxidize the same amount of toluene. However, nitrate salts are far more soluble than oxygen, so nitrate can be added to ground water in high concentrations.

The concentration at which nitrate can be added is limited by the facts that (1) nitrate has a drinking water MCL of 45 mg/L, so that regulatory approval is required for its injection at high concentrations, and (2) nitrogen gas is a product of the toluene degradation and has limited solubility in water. The stoichiometric equation above has assumed that the only nitrogen-containing product of the reaction is N_2, nitrogen gas. Actually, the dissimilative reduction of nitrate to nitrogen by anaerobic bacteria involves a series of intermediate nitrogen-containing compounds, including nitrite (NO_2^-), nitrogen oxide (NO), and nitrous oxide (N_2O) [Brock et al., 1997]. Under different conditions, the rate of utilization of these intermediates can differ [cf., Kuhn, et al., 1988; Major et al., 1988; Dolfing et al., 1990; Flyvbjerg et al., 1993; Elmen et al., 1997]. Although there are some organisms for which N_2O is the end product of nitrate reduction, in general the final product will be N_2 [Brock et al., 1997]. Therefore, equation (2) above is representative. Under this condition, a practical limit for nitrate introduction into ground water might be around 80 mg/L; above about 88 mg/L. The stoichiometry above suggests that nitrogen gas would be formed in excess of its aqueous solubility, and nitrogen gas bubble formation could potentially alter the hydraulic character of the aquifer. Also, it might be difficult to obtain regulatory approval of nitrate injection at concentrations higher than 80 - 100 mg/L.

Toluene, ethylbenzene, meta-xylene, and para-xylene have been observed to degrade under denitrifying conditions [e.g., Ball and Reinhard, 1996]. However, ortho-xylene might degrade only due to cometabolism with toluene or another primary substrate [Evans et al., 1991; Alvarez and Vogel, 1995; Ball and Reinhard, 1996], and benzene might be recalcitrant under denitrifying conditions [Kuhn et al., 1988; Evans et al., 1991; Barbaro et al., 1992; Ball and Reinhard, 1996]. Degradation of the BTEX compounds under denitrifying conditions is often observed to occur sequentially, generally with toluene degraded first and the other compounds following.

Sulfate is commonly found in shallow ground water aquifers, especially those influenced by marine geochemical conditions. Under sulfate-reducing conditions, the stoichiometry for the biodegradation of toluene is

$$C_7H_8 + 4.5\ SO_4^{2-} + 3\ H_2O \rightarrow 2.25\ HS^- + 2.25\ H_2S + 7\ HCO_3^- + 0.25\ H^+ \qquad (3)$$

where cell growth has again been ignored. According to this stoichiometry, the biodegradation of 1 mg/L toluene requires the presence of 4.7 mg/L sulfate. Like nitrate, sulfate can be added to ground water in high concentrations. However, the oxidation of toluene via sulfate reduction results in the production of sulfide, which is known to inhibit the reaction at sufficiently high concentrations [Beller and Reinhard, 1995]. Therefore, there may be a practical limitation to the amount of sulfate that can be added as an alternate electron acceptor. It is known that benzene, toluene, and the three xylene isomers can be degraded under sulfate-reducing conditions [Edwards and Grbic-Galic, 1992; Edwards et al., 1992; Lovley et al., 1995], although the benzene degradation appears to be inhibited by the presence of other BTEX compounds [Edwards et al., 1992; Edwards and Grbic-Galic, 1992; Ball and Reinhard, 1996]. It does not appear that organisms found in Seal Beach aquifer materials are able to degrade ethylbenzene under sulfate-reducing conditions [Edwards et al., 1992; Ball and Reinhard, 1996]. As with denitrifying systems, degradation of the BTEX compounds under sulfate-reducing conditions is often observed to occur sequentially, generally with toluene degraded first and the other compounds following.

Aromatic hydrocarbons including benzene and toluene have also been observed to degrade under fermentative/methanogenic conditions [Wilson et al., 1986; Grbic-Galic and Vogel, 1987]. However, BTEX fermentation is poorly understood. Under fermentative conditions, no external electron acceptor is required, because microorganisms use the substrate (i.e., one or more of the BTEX compounds) as both an electron donor and an electron acceptor. The products of fermentation can include carbon dioxide, organic acids (e.g., acetic acid, propionic acid), alcohols (e.g., ethanol), and/or hydrogen gas [National Research Council, 1993]. Fermentation products are biodegraded by other species of bacteria, ultimately resulting in the production of carbon dioxide, methane, and water. The net stoichiometry for the degradation of toluene under these conditions is

$$C_7H_8 + 5\ H_2O \rightarrow 2.5\ CO_2 + 4.5\ CH_4 \qquad (4)$$

where cell growth has again been ignored. Methanogenesis is inhibited by the presence of other electron acceptors or oxidants (e.g., oxygen, nitrate, or sulfate) and so only occurs in very reduced environments. During some parts of the fermentation/methanogenesis process, carbon dioxide or bicarbonate might be consumed as an electron acceptor; however, the net reaction results in production of carbon dioxide. According to this stoichiometry, the degradation of 1 mg/L toluene results in the production of about 0.78 mg/L methane. Methane gas has limited solubility in water (about 20 mg/L), so degradation of large amounts of contaminant via fermentation/methanogenesis could lead to the formation of methane gas bubbles, thus affecting the hydraulic characteristics of the aquifer.

Because of the biological and physico-chemical limitations associated with individual electron acceptors, one possibility for enhanced bioremediation is to augment the contaminated zone with the maximum capacity of several electron acceptors simultaneously. Under such conditions, the electron acceptors would be used sequentially according to decreasing energy yield. If there is ground water flow, the result will be a spatial variation in geochemical conditions downgradient of the point of electron acceptor injection. Because oxygen is the preferred electron acceptor, the aerobic zone will develop first, followed by a nitrate-reducing zone, a sulfate-reducing zone, and finally a fermentative/methanogenic zone. When using multiple electron acceptors, the limitations of each individual electron acceptor must be considered with respect to solubility limitations and potential chemical and biological interactions. Furthermore, it is difficult to accelerate methanogenic degradation of BTEX compounds via injection of electron acceptors, because the contaminant serves as both electron donor and acceptor. Methanogenic degradation would be expected to be a significant process only where other electron acceptors (oxygen, nitrate, sulfate) have already been depleted.

In the project described in this report, our goal was not only to demonstrate an enhanced bioremediation technology, but also to quantify anaerobic degradation processes and to evaluate the efficacy of augmentation with multiple electron acceptors. In order to properly control the geochemical conditions, we did not employ the maximum capacity of multiple electron acceptors. Rather, we established three distinct treatment zones, each with its own type of geochemical conditions. This is discussed further in Section 2.1.2, below.

2.1.2 Engineering Process: In order to achieve both of the objectives of this project (see Section 1.3), a system of injection and extraction wells was installed at a contaminated site. Because one of the goals of this project was to quantify the efficacy of individual anaerobic degradation processes, the system was operated in a manner different from how it would likely be operated at a "typical" contaminated site. In this section, we note some of the particular aspects in which our operation differs from the recommended operation at other contaminated sites.

In order to compare anaerobic degradation under three different types of geochemical conditions, one extraction well and three injection wells were installed in the most highly contaminated region of the site. Each injection well was used to set up a subsurface treatment zone with particular geochemical conditions. In each of the three zones, four monitoring wells were installed. An additional monitoring well was placed approximately 7 m upgradient of each of the three zones. Figures 3 and 4 show a plan view of the contaminated site and show the positions of

the extraction well, the injection wells, and the monitoring wells. Slug tests indicated a slow ground water velocity, about 0.7 cm/day, in the direction indicated on Figure 4.

Figure 5 shows a schematic of the injection/extraction well system. Samples were taken at monitoring wells located between the injection well and the extraction well in order to measure the concentrations of the electron acceptors and of the target contaminants.The extraction well was used to remove water that contained either the target contaminants (in this case, BTEX) or compounds that inhibit the bioremediation process (e.g., sulfide). The extracted water was treated to remove the compounds of concern, then augmented with electron acceptors in order to stimulate biodegradation of the target contaminants, then re-injected into the contaminated region of the aquifer. In the demonstration described in this report, we utilized treatment and augmentation systems that were unusual in the following respects:

(1) The treatment system was designed to remove not only target contaminants and inhibitory products, but also excess electron acceptors (oxygen, nitrate, and sulfate). This was done in order to provide careful control over the composition of the re-injected water so that we could investigate the effects of particular geochemical conditions on the bioremediation process. Under typical operating conditions at a full-scale remediation site, excess electron acceptors would not be removed prior to augmentation and re-injection.

(2) The augmentation system did not always provide the optimum mixture of electron acceptors for bioremediation. For instance, no oxygen was added during this demonstration. This was done because one of the goals of the project was to compare bioremediation under controlled anaerobic conditions (denitrifying, sulfate-reducing, and methanogenic).

(3) During the early portions of the demonstration, a tracer (bromide) was injected in order to establish the hydraulic conditions and in order to estimate travel times between the injection wells and the monitoring wells.

Each injection well was fully screened across the saturated zone of the aquifer and was located 10 m away from the extraction well. The extraction well was also fully screened across the saturated zone. The rate of injection in each well was about 1.5 L/min; the rate of extraction was about 4.5 L/min. Extracted water went through a treatment system to remove hydrocarbons, gases (including oxygen, methane, and nitrogen), and anions (including nitrate, sulfate, and sulfide). After treatment, the water was split into three streams. Each stream was sent to the one of the injection wells, where it was augmented with the appropriate electron acceptor(s): sulfate for injection well 2, sulfate and nitrate for injection well 4, and neither for injection well 3. In this manner, three different treatment zones with different geochemical conditions were established between the injection wells and the extraction well. These three zones are labeled zones 2, 3, and 4, according to the number of the injection well pertaining to each zone (see Figure 4). Zone 3 was expected to develop fermentative/methanogenic conditions; zone 2 was expected to develop first sulfate-reducing and then fermentative/methanogenic conditions; zone 4 was expected to develop first denitrifying, then sulfate-reducing, then fermentative/methanogenic conditions. We chose to install three injection wells and one extraction well in order to compare anaerobic degradation under these three different types of treatments; if this technology were

employed at a full-scale remediation site, either more or fewer injection and extraction wells could be installed, and the geochemical conditions could be optimized for the particular site.

Each of the monitoring wells was in fact a well bundle consisting of seven monitoring points. The wells were composed of seven 0.1875-inch stainless steel tubes, spaced vertically at distances of 14 inches apart. In each monitoring well, the top tube was placed very close to the water table; the bottom tube was located about 7 feet below the water table, with the middle five tubes spaced evenly in between. As shown in Figure 4, each of the three treatment zones had five multilevel sample bundles associated with it. For each zone, one multilevel sample well was located approximately 7 m updgradient of the injection well, and two multilevel sample wells were located 2 and 4 m in the direction of the extraction well. In zones 2 and 3, additional monitoring wells were placed 2 and 4 m downgradient from the injection well. In zone 4, where the injection well was directly upgradient of the extraction well, monitoring wells were placed 2, 4, 6, and 8 m from the injection well.

Sampling was performed automatically via an Automated Sampling and Analysis Platform (ASAP) from Analytic and Remedial Technology (Milpitas, CA). Connections between the monitoring wells and the ASAP were stainless steel tubing. After flushing the sample lines, the ASAP extracted a sample and prepared separate aliquots for analysis of:

(1) Concentrations of volatile organic compounds (including BTEX) via a modified purge-and-trap method with gas chromatography (GC), photo-ionization detection (PID), and flame ionization detection (FID)
(2) Concentrations of anions (including bromide, sulfate, and nitrate) via ion chromatography
(3) pH, dissolved oxygen, and concentration of sulfide via specific probes.

Results from the ASAP analyses were automatically logged in a computer database. Additional details about the ASAP are provided in the Technology Demonstration Plan [Appendix B] and in the Quality Assurance Project Plan [Appendix C].

The system could be operated in three modes: (1) injection/extraction with no augmentation of electron acceptors, i.e., flushing of the treatment zones with unaugmented treated water; (2) injection/extraction with augmentation of electron acceptors in the injection wells; and (3) no flow, i.e., both injection and extraction wells are off. A treatment cycle generally consisted of operating in these three modes sequentially. First, the treatment zones were flushed with water that had been treated to remove hydrocarbons, gases, and anions, but that had not been augmented with electron acceptors. This served to remove inhibitory products, to remove background concentrations of the electron acceptors, and to reduce the initial BTEX concentration in each zone. The flushing stage was implemented mainly to establish base-line conditions in the treatment zones for evaluation purposes; at a full-scale implementation of this technology, the flushing stage might be omitted depending on whether or not inhibitory by-products were present. The second stage of the treatment consisted of injecting the zones with water that had also been augmented with the appropriate electron acceptor(s), in order to stimulate biological activity. Third, the injection and extraction wells were shut off, and the

system was monitored while in a no-flow mode to see how the target contaminants responded to the established geochemical conditions. Like the flushing stage, the no-flow stage might be omitted in a full-scale implementation of the technology; here it was necessary for evaluation purposes. Over the course of a 4-week augmentation stage, about 180,000 L water was extracted, and about 60,000 L water was injected into each treatment zone. This was sufficient to establish treatment zones of about 150–200 m^3 in size (assuming an aquifer porosity of 0.3–0.4). A conservative tracer, such as bromide, could be added during the flushing period or during the augmentation period to ensure good hydraulic connection between the injection wells and the monitoring wells.

Some of the key design criteria for this technology are:

- Number and location of extraction and injection wells
- Injection and extraction flow rates
- Method of treating extracted water
- Choice of electron acceptors to be injected
- Concentration of electron acceptors injected
- Duration of flushing, augmentation, and no-flow periods

Values chosen for these design parameters will vary depending on site-specific conditions.

2.2 Strengths, Advantages, and Weaknesses of this Technology

Compared to conventional pump-and-treat remediation, the main advantages to in situ bioremediation (both aerobic and anaerobic) are:

(1) Contaminants are mineralized in situ, thereby avoiding the physical removal of the solids laden with toxic contaminants and the above-ground treatment of large volumes of water.
(2) In situ bioremediation produces little or no volume of secondary waste streams that need to be treated and disposed of.
(3) Contaminants are transformed to harmless products, not just transferred to a different phase (e.g., activated carbon).
(4) By maintaining a low contaminant concentration in the ground water, high rates can be maintained for contaminant desorption from aquifer solids and contaminant dissolution from residual non-aqueous liquid phases, thereby shortening overall clean-up times.

The main advantages of anaerobic bioremediation over aerobic bioremediation are:

(1) Alternate electron acceptors such as nitrate or sulfate are more water soluble than oxygen, and consequently allow more rapid supply of electron acceptors to the aquifer.

(2) Anaerobic bacteria produce less biomass than aerobic bacteria, and therefore are expected to cause fewer problems with aquifer clogging, especially near injection wells.
(3) The use of anaerobic bacteria takes advantage of intrinsic processes which occur naturally without intervention.
(4) Factors (1)–(3) should result in considerable cost savings.

Challenges to the application of anaerobic biodegradation include:

(1) The process is still not thoroughly understood, especially under field conditions, making clean-up times difficult to predict.
(2) Because there is little operational experience with anaerobic bioremediation, the process is not always considered acceptable by regulators.
(3) Benzene, the most toxic of the BTEX compounds, has not conclusively been shown to degrade under all anaerobic conditions that exist in the field.
(4) The efficacy for some gasoline additives (e.g., MTBE) has yet to be determined.

Anaerobic biodegradation is also subject to some impediments that affect other treatment technologies:

(1) Contaminants that are sorbed to aquifer solids or are present in a non-aqueous liquid phase must first be transferred to the aqueous phase before they can be treated. This mass transfer process can limit the rate of nearly all types of treatment technologies.
(2) Electron acceptors that are introduced via injection wells will tend to flow preferentially into regions of high conductivity, leaving contamination in low-conductivity regions untreated. The presence of contamination in low-conductivity regions is also an impediment to pump-and-treat remediation, aerobic bioremediation, air sparging, and other remediation techniques.
(3) When electron acceptors are introduced via injection well, the injected water can push out the contaminated water, preventing adequate mixing of contaminants and electron acceptors. This can also be an impediment to any remediation technique that uses aqueous-phase chemical injection (e.g., aerobic bioremediation).
(4) Contaminants that are commonly found in conjunction with fuel hydrocarbons, such as the gasoline additive methyl *tert*-butyl ether (MTBE), often biodegrade very slowly under either aerobic or anaerobic conditions.

Currently, other anaerobic in situ bioremediation techniques are frequently considered for the remediation of fuel hydrocarbons. One of these is intrinsic bioremediation, as discussed in Section 1.1. Intrinsic bioremediation relies on the natural ground water flow to supply sufficient electron acceptors for mineralization of contaminants, and to remove any inhibitory metabolic products that are formed. The main advantage of intrinsic bioremediation over enhanced bioremediation is that it is less expensive, since injection wells are not needed and no chemicals need to be supplied. However, intrinsic bioremediation might not be sufficient to degrade the target contaminants in all cases, and is almost always slower than enhanced biodegradation,

especially at sites where the ground water flow is slow, such as the Naval Weapons Station Seal Beach site.

2.3 Factors Influencing Cost and Performance

Table 1 shows the design and operational parameters that affect the cost and performance of the technology, as explained in the Federal Remediation Technologies Roundtable (FRTR) *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* [1998]. These parameters were also identified in Table 5 of the Technology Demonstration Plan [Appendix B].

Table 1: Operating Parameters Affecting Treatment Cost and Performance

Parameter	Range of Values
Injection Well Flow Rate	1.5 L/min in each zone
Extraction Well Flow Rate	sum of injection rates
pH of Ground Water	6–9 pH units
Nitrate Concentration in Feed Water	15–120 mg/L
Sulfate Concentration in Feed Water	15–120 mg/L

3. Site/Facility Description

3.1 Background

The site for this demonstration was the Naval Weapons Station (NWS) Seal Beach, located in southern California (Figures 1, 2). The NWS Seal Beach is located on the transition of geologic formations called Landing Hill and the Sunset Gap. The physiographic and hydrogeologic setting are described in detail by Schroeder [1991]. A gasoline station located on the premises of the weapons station is contaminated with fuel hydrocarbons that leaked from a steel underground storage tank. The leak was discovered in 1984. The weapons station also contains the Seal Beach National Wildlife Refuge, a wetlands marsh located in the Sunset Gap formation. An investigation by the U.S. Geological Survey [Schroeder, 1991] found that the contamination from the leaking tank had migrated to the ground water underlying the Refuge. The Navy's concern about the possible adverse effects of the contamination on the Wildlife Refuge made the Seal Beach facility a potential site at which to demonstrate this remediation technology.

Furthermore, the following conditions made the NWS Seal Beach site especially well suited for this demonstration:

(1) The ground water in the contaminated zone had been anaerobic for at least a decade. Both laboratory and field studies had demonstrated the presence of anaerobic bacteria that are capable of degrading fuel hydrocarbons.
(2) The aquifer is shallow and the cost of placing wells is relatively low.
(3) At some sites where the ground water is contaminated with fuel hydrocarbons, the prevailing ground water flow may supply sufficient doses of electron acceptors and remove inhibitory products at rates that render engineered simulation unnecessary. At the Seal Beach site, however, the regional ground water velocity is very small. Previous studies at the site [Reinhard et al., 1997] indicate that the supply of electron acceptors and/or the removal of inhibitors are limiting, suggesting the need for enhancement of intrinsic bioremediation processes.
(4) The aquifer solids are sufficiently permeable to allow pumping of at least a few gallons per minute, i.e., transmissivity is higher than 2 ft^2/day. The interbedding of clay lenses within silty sand (possibly sandy silt) is typical for alluvial deposits along the California Coast.
(5) The regulatory agency, the California Regional Water Quality Control Board (CRWQCB), has been supporting research at this site for many years, including controlled release experiments.
(6) Laboratory and field data from previous studies [Haag et al., 1991; Edwards et al., 1992; Edwards and Grbic-Galic, 1992; Ball and Reinhard, 1996; Reinhard et al., 1997] had suggested the probability of success of such a demonstration at the Seal Beach site.

Table 2 summarizes some of the characteristics of the site, in the format suggested by the Federal Remediation Technologies Roundtable (FRTR) *Guide to Documenting Cost and Performance*

for Remediation Projects [1995], and as documented previously in Table 3 of the Technology Demonstration Plan [Appendix B].

Table 2: Standard Terminology for the Demonstration Site
Site Background:
Historical Activity that Generated Contamination:
Leaking underground storage tank
Management Practices that Contributed to Contamination:
Underground storage tank (fuel)
Site Characteristics:
Media Treated:
Ground water
Soil (in situ)
Light nonaqueous-phase liquids (LNAPL)
Contaminants Treated:
Organic Compounds, Volatile, Non-halogenated: BTEX
Organic Compounds, Petroleum Hydrocarbons
Treatment System:
Primary Treatment Technology:
Soil (in situ): Bioremediation
Ground water (in situ): Bioremediation
Supplemental Treatment Technology:
Pre-treatment: Nutrient (electron acceptor) injection
Post-treatment: Carbon adsorption, Ion exchange, Gas stripping

3.2 Site/Facility Characteristics

The hydrogeology of the NWS Seal Beach has been described in detail by Schroeder [1991]. About 5800 gallons of fuel leaked from an underground storage tank and contaminated the soil and ground water in the region, as shown in Figure 3. The leak was discovered in 1984 when the steel storage tank was being replaced by a pair of fiberglass tanks. Between 1984 and 1996, observation wells monitored by the Orange County Water District indicated that the contaminant plume in the ground water was retracting, and by the beginning of this demonstration, the plume was concentrated around the source area.

In June 1995, a water sample was taken in this region from a well screened near the water table. The sample produced the following concentrations for BTEX compounds: 14.1 mg/L benzene, 13.9 mg/L toluene, 2.7 mg/L ethylbenzene, 8.3 mg/L combined meta- and para-xylene, 4.5 mg/L ortho-xylene. Some monitoring wells showed the presence of a non-aqueous liquid phase. Because the non-aqueous phase is less dense than water, it tends to spread on top of the water

table, and saturated-zone BTEX concentrations tend to be higher near the water table than they are several feet below the water table.

The ground water velocity in the region is low, approximately 0.7 cm/day. The ground water flow rate and direction might fluctuate somewhat with the season and with the tides.

Table 3 shows the site characteristics that affect the treatment cost and performance, as specified by the Federal Remediation Technologies Roundtable (FRTR) *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* [1998].

Table 3: Matrix Characteristics Affecting Treatment Cost and Performance

Parameter	Value	Measurement Procedure
Soil Types (Soil Classification and Clay Content)	See well logs in Appendix D. Here we give the extraction well as an example. 0–2 feet below ground surface (BGS): silty, fine to coarse sand 2–4 ft BGS: silty clay 4–5 ft BGS: silty, medium to coarse sand 5–8 ft BGS: coarse sand, some gravel 8–10 ft BGS: silt 10–12 ft BGS: silty fine sand 12–14 ft BGS: fine to medium sand 14–14.5 ft BGS: silty clay 14.5–15 ft BGS: medium sand	visual inspection by well logger, reviewed by registered geologist
Hydraulic Conductivity	0.0005–0.002 cm/sec	pump tests on 6 wells
pH	6.9–8.2 (usually 7.1–7.8) pH units	pH probe
Total Organic Carbon	0.015%–0.028%, bulk value 0.024%	
Non-aqueous phase liquids (NAPL)	Yes, light (less dense than water)	Found in monitoring wells

4. Demonstration Approach

4.1 Performance Objectives

This project was intended to meet two broad goals:

(1) Demonstration of a technology by which contaminants are removed from ground water via enhanced in situ anaerobic biodegradation
(2) Detailed documentation of the anaerobic biodegradation of fuel hydrocarbons under three different types of geochemical conditions.

In keeping with these two primary goals, the demonstration focused on the use of alternate electron acceptors (i.e., electron acceptors other than oxygen) for in situ bioremediation of hydrocarbon fuel contaminants. It is important to note that, because one of the goals of this project was a detailed evaluation, the remediation technology was operated under carefully controlled conditions, sometimes at conditions that were known to be less than optimal. This was done in order to collect data for the evaluation of anaerobic biodegradation processes. The performance objectives by which the success of this project is measured must take into consideration the dual goals of the project.

The technology design used an injection/extraction well doublet (Figure 5). The extraction well is used to remove compounds that inhibit the bioremediation; it is also used as a source of water that can be treated, augmented with electron acceptors, and then supplied to the contaminated zone via the injection wells.

The principal performance criterion for this demonstration is the historical change in contaminant concentrations as measured in the monitoring wells, which are located between the injection well and the extraction well (Figures 4 and 5). The target compounds for this demonstration are benzene, toluene, ethylbenzene, and xylene, collectively known as BTEX. The drinking water maximum contaminant levels (MCLs) for the BTEX compounds are, respectively, 5 parts per billion (ppb), 1 part per million (ppm), 0.7 ppm, and 10 ppm.

The secondary performance criterion for this technology is based on the measured concentrations of electron acceptors and of metabolic products. This secondary criterion is used to further validate the degradation of the contaminants.

In addition to these two performance criteria, the Technology Demonstration Plan [Appendix B] identified the following technical issues to be evaluated with regard to the technology's performance:

(1) Disposal of a process waste stream
(2) Reliability of anaerobic bioremediation, particularly with regard to

(a) Presence and viability of anaerobic bacteria capable of growing on BTEX compounds under field conditions, which might include a limited supply of nutrients or the build-up of toxic by-products
(b) Reliability of hardware used for recirculating water through the treatment zone, which might be susceptible to plugging caused by excessive biomass formation, precipitation, or gas formation

(3) Ease of use, i.e., how much individual training, preliminary investigation, or special precautions are needed to implement this technology
(4) Versatility, i.e., how easily the technology can be applied to remove contaminant groups other than BTEX or fuel hydrocarbons
(5) Off-the-shelf procurement, i.e., are the hardware and software for this technology easily obtained
(6) Maintenance, especially of

(a) Injection and extraction flows
(b) Water quality in the feed stream
(c) Treatment system for extracted water
(d) Electron acceptor feed solution

(7) Scale-up issues, i.e., how easily this technology might be applied to larger-scale sites.

4.2 Physical Set-up and Operation

The treatment system consisted of one extraction well and three injection wells, with relative locations as indicated in Figure 4. Different electron acceptors were added at each injection well, creating three different treatment zones with different geochemical sequences. Zone 3 received no augmentation of electron acceptors, and was therefore expected to develop methanogenic conditions; zone 2 was augmented with sulfate, and was expected to develop first sulfate-reducing and then methanogenic conditions; zone 4 was augmented with nitrate and sulfate, and was expected to develop first denitrifying, then sulfate-reducing, then methanogenic conditions. The three injection wells were installed in locations of moderate BTEX contamination; the extraction well was installed in a region of relatively high contamination. Details of the well design are provided in the Technology Demonstration Plan [Appendix B]. As noted previously, the three zones were established in this manner specifically because one of the objectives of this project was to evaluate the efficacy of anaerobic biodegradation under different geochemical conditions. A full-scale implementation of this technology might employ a different number of injection/extraction wells, and might inject different levels of electron acceptors in order to optimize the bioremediation.

A treatment evaluation consisted of three stages. First, the three treatment zones were flushed with water that had been treated to remove hydrocarbons, gases, and anions, but had not been augmented with electron acceptors. This served to remove inhibitory products, to remove background concentrations of the electron acceptors, and to reduce the initial BTEX concentration in each zone. The flushing stage was implemented mainly to establish base-line

conditions in the treatment zones for evaluation purposes; at a full-scale implementation of this technology, the flushing stage might be omitted depending on whether or not inhibitory by-products are present. The second stage of a treatment evaluation consisted of injecting the zones with treated water that had also been augmented with the appropriate electron acceptor(s). The augmentation stage lasted for about 4–5 weeks, which was sufficient time to develop treatment zones of about 180 m^3 in size. The third stage was a no-flow stage, in which both injection and extraction wells were shut off. During this time, the treatment zones were monitored to determine how the BTEX concentrations in each zone responded to the established geochemical conditions.

This technology demonstration lasted about 17 months and consisted of three treatment evaluations. The first augmentation period ran from 9/14/97–10/16/97; the second augmentation ran from 5/24/98-6/23/98; the third augmentation period ran from 9/2/98–10/14/98. For all three treatment evaluations, the injection flow rate was about 1.5 L/min in each well, and the extraction flow rate was about 4.5 L/min. The third augmentation was not preceded with a flushing stage. Each augmentation consisted of different concentrations of electron acceptors being injected, as summarized in Table 4. A conservative tracer was injected during the flushing period of the first treatment evaluation in order to establish that the monitoring wells were hydraulically connected to the injection wells.

Table 4: Injected Electron Acceptor Concentrations During Treatment Evaluations

Evaluation #	Zone 2	Zone 3	Zone 4
1	15–20 mg/L sulfate	no electron acceptors added	15 mg/L nitrate, 15 mg/L sulfate
2	70–90 mg/L sulfate	no electron acceptors added	45–55 mg/L nitrate, 70–80 mg/L sulfate
3	40–50 mg/L nitrate, then 75–95 mg/L sulfate	no electron acceptors added	85–125 mg/L nitrate, 70–100 mg/L sulfate

Figure 5 shows a schematic for the ground water recirculation system used in this demonstration. Figure 6 shows a schematic for the water treatment system that is used to remove hydrocarbons, gases, and anions from the extracted water before it is augmented with electron acceptors and re-injected. Figure 7 shows a schematic for how the treated water is split into three streams and augmented with the appropriate electron acceptor(s). We utilized treatment and augmentation systems that were unusual in the following respects:

(1) The treatment system was designed to remove not only target contaminants and inhibitory products, but also excess electron acceptors (oxygen, nitrate, and sulfate). This was done in order to provide careful control over the composition of the re-injected water so that we could investigate the effects of particular geochemical conditions on the bioremediation process. Under typical operating conditions at a full-scale remediation site, excess electron acceptors would not be removed prior to augmentation and re-injection.

(2) The augmentation system did not always provide the optimum mixture of electron acceptors for bioremediation. For instance, no oxygen was added during this

demonstration. This was done because one of the goals of the project was to compare bioremediation under three different types of anaerobic conditions (denitrifying, sulfate-reducing, and methanogenic).

The flushing and augmentation stages typically lasted 4–5 weeks. During these stages, the injection/extraction system was operated all 24 hours per day, and one operator was present at the site at all times to maintain the water treatment system and to ensure that the injection, extraction, and sampling ran properly. During the no-flow stages, only periodic maintenance was required.

During the treatment demonstration, low-volume waste streams were produced from various sources. Ion exchange was used to remove anions from the extracted water prior to augmentation and re-injection; the brine produced from regenerating the ion exchange columns represented one waste stream. Spent activated carbon (used to remove hydrocarbons from the extracted water) represented a second waste stream. In addition, the analytical system and the injection system produced a waste stream of less than 0.5 L/min. In a typical application of this technology, where sampling and analysis would be performed less frequently, this waste stream would be even lower volume.

4.3 Sampling Procedures

Sampling was performed automatically via an Automated Sampling and Analysis Platform (ASAP) from Analytic and Remedial Technology (Milpitas, CA). The automated on-line sampling manifold consisted of 111 sample ports, of which 105 ports were connected directly to the multi-level sample bundles of the monitoring wells. Connections were 0.1875-inch stainless steel sample lines. The remaining six ports were connected to the treatment system and to the three injection wells. After flushing the sample lines, the ASAP extracts a sample and prepares separate aliquots for analysis of volatile organic compounds, anions, pH, and dissolved oxygen. The ASAP provided samples directly to the instrumentation without operator intervention and was operated continuously from August 1997 until November 1998. Sample waste water was recycled back to the inlet of the water treatment system.

Each of the three treatment zones had five monitoring wells, as shown in Figure 4. Each monitoring well consisted of seven 0.1875-inch stainless steel tubes with the inlets spaced vertically 14 inches apart, thus providing seven discrete sample locations covering the length of the injection well screens at each monitoring well location. The inlet of each sample tube was enclosed in glass wool filter protected by nylon "horse hair" fabric, a double weave knit. The monitoring wells were installed by placing the sample bundles in 2-inch boreholes and backfilling with sand; this minimizes the required flush volumes required to obtain representative samples. Additional details on the sampling procedure can be found in the Technology Demonstration Plan [Appendix B] or in the Quality Assurance Project Plan [Appendix C].

4.4 Analytical Procedures

Connections between the monitoring wells and the ASAP were stainless steel tubing. After flushing the sample lines, the ASAP extracted a sample and prepared separate aliquots for analysis of :

(1) Concentrations of volatile organic compounds (including BTEX) via a modified purge-and-trap method with gas chromatography (GC), photo-ionization detection (PID), and flame ionization detection (FID);
(2) Concentrations of anions (including bromide, sulfate, and nitrate) via ion chromatography; and
(3) pH, dissolved oxygen, and concentration of sulfide via specific probes.

Although the modified purge-and-trap system is not of the design used in standard methods, it has been demonstrated successful by the U.S. Environmental Protection Agency [U.S. EPA, 1993]. The gas chromatograph was not able to resolve meta- and para-xylene, so the concentrations of these two compounds were measured as a sum. Photo-ionization detection was used for the measurement of BTEX concentrations; flame ionization detection was used for the measurement of the concentrations of aliphatic hydrocarbons.

Results from the ASAP analyses were automatically logged in a computer database. All samples were stamped with date and time, and had unique names for sample locations. Additional details about the analytical procedure are provided in the Technology Demonstration Plan [Appendix B] and in the Quality Assurance Project Plan [Appendix C].

Table 5: Compounds Analyzed by Automatic Sampling and Analysis Platform

Compound	Gas Chromatography	Ion Chromatography	Specific Probe
Methane	X		
3-methyl-pentane	X		
Hexane	X		
Benzene	X		
Toluene	X		
Ethylbenzene	X		
Xylenes	X		
Trimethyl-benzenes	X		
Chloride		X	
Bromide		X	
Nitrate		X	
Sulfate		X	
Dissolved Oxygen			X
pH			X
Sulfide			X

5. Performance Assessment

5.1 Performance Data

As discussed in Section 4.1, above, the evaluation of the technology's performance is based primarily on the historical change in contaminant (BTEX) concentrations, and secondarily on the historical change in electron acceptor concentrations. These concentrations were measured through monitoring wells. Each monitoring well had seven sampling points, spaced vertically about 14 inches apart. Each sampling point had a unique name that is given in three parts: the first part indicates in which treatment zone the monitoring well is located; the second part indicates the number of the well bundle within the zone (see Figure 4); and the third part indicates the vertical location of the sampling point, where "1" indicates the uppermost sampler and "7" indicates the lowest sampler. For example, a designation "4-B1-5" means zone 4, well bundle 1, the fifth sampler from the top. The injection wells are designated "I2," "I3," and "I4," as indicated in Figure 4.

In the subsections below, we present data showing the historical response of the BTEX contaminants and of the electron acceptors. Contaminant histories are presented in Figures 8–24. On many of these figures, different periods in time are labeled with the letters "F," "A," or "N." These letters correspond to the three stages of a treatment evaluation: "F" indicates the first (flushing) stage, in which the treatment zone was flushed with treated but unaugmented water; "A" indicates the second (augmentation) stage, in which the treatment zone was augmented with electron acceptors; and "N" indicates the third (no-flow) stage, in which the injection and extraction wells were shut off such that there was no flow through the treatment zones.

5.1.1 Benzene Concentration History: Figure 8 shows the change in benzene concentration with time, as measured at monitoring points 3-B1-5 and 4-B1-5. These two monitoring wells were chosen for comparison because they are located at approximately the same vertical location, a few feet below the water table, but in different treatment zones. In both monitoring wells, the benzene concentration was initially in the range 3–5 mg/L, but decreased rapidly during the initial flushing stages. At the end of the first augmentation (10/14/97), the concentration in each well was about 1 mg/L. However, during the first no-flow stage, the benzene concentration rebounded in both wells: to about 2 mg/L in 4-B1-5, and to over 5 mg/L in 3-B1-5. This rebound is very commonly seen in pump-and-treat remediation systems when the pumping is temporarily shut down. It can be caused by:

(1) Dissolution of benzene from globules of non-aqueous phase liquid into the aqueous phase
(2) Desorption of benzene from aquifer solids into the aqueous phase
(3) Molecular diffusion of benzene from a region of the aquifer where the aqueous concentration is still very high
(4) Slow flow of ground water into the test zone from a more contaminated region.

It is very difficult to speculate which of these causes might be primarily responsible. It is perhaps significant that the rebound was much stronger in zone 3 (where no electron acceptors were added) than in zone 4 (which was augmented with nitrate and sulfate); this could be an indication that the addition of electron acceptors suppressed the rebound effect by stimulating biological degradation of benzene. However, there are numerous other reasons why the four rebound mechanisms listed above might be stronger in zone 3 than in zone 4; therefore, the suppressed rebound in zone 4 should not necessarily be interpreted as in indication of biodegradation of benzene.

During the second treatment cycle, similar behavior was observed. The concentrations decreased rapidly during the flushing stage, decreased slowly during the augmentation stage (which could be due either to biological activity or to the continued flushing that occurs during this stage), then rebounded during the no-flow stage. As before, the rebound was stronger in zone 3 than in zone 4. In both zones, the rebound was weaker in the second treatment cycle than in the first treatment cycle. This is not surprising, because the additional flushing in the second treatment cycle would have removed some of the benzene mass, weakening the rebound mechanisms listed above.

In the third treatment cycle, no flushing stage preceded the augmentation. Benzene concentrations dropped during the augmentation stage and did not rebound during a short no-flow stage. The final benzene concentration was higher in zone 3 than in zone 4. In both zones, the final benzene concentration was much lower than initial concentration. In zone 3, the benzene concentration dropped from over 4 mg/L to about 0.3 mg/L, and in zone 4, the benzene concentration dropped from about 3 mg/L to about 0.05 mg/L.

To summarize these observations, the benzene concentrations in the ground water did drop considerably during the 17-month demonstration period. However, it appears that most of the benzene removal was probably due to flushing; there may have been some benzene removal from biodegradation, but the data are inconclusive. Benzene was removed more effectively from zone 4 than from zone 3. This could be an indication that augmentation with electron acceptors improves benzene removal, but it might merely be an indication that zone 3 had a higher residual saturation or was more susceptible to encroachment from highly contaminated regions of the site. Qualitatively, these results are consistent with previous studies [e.g., Acton and Barker, 1992; Edwards et al., 1992; Thierrin et al., 1995; Ball and Reinhard, 1996; Reinhard et al., 1997] that have shown benzene to be relatively resistant to biological degradation under anaerobic conditions.

5.1.2 Toluene Concentration History: Figure 9 shows the change in toluene concentration with time at point 4-B1-5; for comparison, the benzene concentration at 4-B1-5 is also shown. Figure 9 clearly shows that the toluene concentration was orders of magnitude lower than the benzene concentration, even at the start of the first flushing stage at the very beginning of the demonstration . In general, toluene was present at high concentrations only near the water table, where there is more residual non-aqueous phase liquid (NAPL) hydrocarbon. A few feet below the water table, the toluene concentration rarely exceeded 50 µg/L at any of the monitoring wells. It appears that toluene was preferentially degraded by the native microbial population, and that this degradation could take place even without augmentation of electron acceptors. This is

consistent with the results from previous laboratory studies with aquifer materials from Seal Beach [Haag et al., 1991; Ball and Reinhard, 1996].

5.1.3 Ethylbenzene Concentration History: Figure 10 shows the change in ethylbenzene concentration with time at location 2-B1-4. For comparison, the benzene concentration at 2-B1-4 is also shown. Figure 10 shows that in zone 2, which was augmented with sulfate, ethylbenzene responded to the treatment in a manner almost identical to benzene, i.e., removal appears to be primarily via flushing. Thus, it appears that augmentation with sulfate did not enhance ethylbenzene degradation. However, an interesting result was seen during the third augmentation (9/2/98–10/14/98): during this augmentation, in which nitrate was added prior to sulfate (see Table 4), the ethylbenzene concentration dropped rapidly. This might be an indication that, whereas augmentation with sulfate had little effect on ethylbenzene concentration, addition of nitrate enhanced ethylbenzene degradation.

Figure 11 is consistent with the hypothesis that addition of nitrate enhances ethylbenzene degradation. Figure 11 shows the benzene and ethylbenzene concentrations at 4-B1-4. Note that there are two scales for the y-axis in Figure 11; the scale on the left-hand side of the graph is for ethylbenzene, and the scale on the right-hand side of the graph is for benzene. Figure 11 shows that, in zone 4, which was augmented with nitrate as well as sulfate, the ethylbenzene concentration steadily declined, reaching a final concentration of less than 50 µg/L. Ethylbenzene appears to have experienced significantly less rebound than benzene, perhaps indicating greater biodegradation of ethylbenzene than of benzene under denitrifying conditions. These results are consistent with previous laboratory studies, which have shown that ethylbenzene can be degraded under denitrifying conditions but not under sulfate-reducing conditions [e.g., Edwards et al., 1992; Ball and Reinhard, 1996].

In zone 3, where fermentative/methanogenic conditions were expected to develop, the ethylbenzene concentration was low even at the beginning of the demonstration. It is therefore difficult to assess the effectiveness of methanogenesis with regard to ethylbenzene removal.

5.1.4 Xylene Concentration History: Figure 12 shows the change in xylene concentration with time at location 2-B1-4. The meta- and para-isomers of xylene were measured as a sum concentration because they co-eluted from the gas chromatograph; ortho-xylene is measured separately because it could be resolved on the gas chromatograph. For comparison, Figure 12 also shows the benzene concentration at 2-B1-4. The m+p-xylene isomers responded in a manner almost identical to benzene, i.e., the sum concentration of m+p-xylene was not effectively reduced by sulfate augmentation. This means that at least one of the meta- and para-isomers was resistant to degradation under sulfate-reducing conditions, and perhaps both isomers were. In contrast, the o-xylene concentration dropped sharply during the first augmentation stage (9/14/97–10/16/97) and never experienced any rebound. It appears that the o-xylene was almost completely transformed due to the addition of sulfate. Previous studies with Seal Beach aquifer material had produced conflicting results regarding the degradation of o-xylene under sulfate-reducing conditions:

(1) Edwards et al. [1992] observed o-xylene mineralization after a lag period and after toluene and p-xylene were degraded.
(2) Ball and Reinhard [1996] observed o-xylene degradation to occur under sulfate-reducing conditions only via co-metabolism with toluene, which is believed to result in (2-methyl-benzyl)-succinate as a dead-end metabolic product [Beller et al., 1995, 1996].
(3) Reinhard et al. [1997] observed toluene and m+p-xylene removal under unamended conditions, and o-xylene removal upon the addition of sulfate.

In this demonstration, toluene concentrations were low at all times, such that it is doubtful that o-xylene transformation was due to co-metabolism with toluene. It is possible that o-xylene was degraded as a primary substrate, or that it was degraded co-metabolically with a primary substrate other than toluene. Samples were not analyzed for the presence of (2-methyl-benzyl)-succinate during this demonstration, so it is difficult to determine if o-xylene was a primary or secondary substrate.

Figure 13 shows the change in xylene and benzene concentrations with time at point 4-B1-5. There are two scales for the y-axis in Figure 13; the scale on the left-hand-side of the graph is for xylene, and the scale on the right-hand-side of the graph is for benzene. Figure 13 shows that, in zone 4, which was augmented with nitrate as well as sulfate, the xylene concentrations steadily declined. Xylene appears to have experienced significantly less rebound than benzene, perhaps indicating greater biodegradation of xylene than of benzene under denitrifying conditions. As in zone 2, the o-xylene isomer disappeared much more readily and rapidly than the m+p-xylene isomers; o-xylene was almost completely removed by the end of the first flushing stage, prior to any augmentation with nitrate or sulfate.

In zone 3, where fermentative/methanogenic conditions were expected to develop, the concentrations of all xylene isomers were very low even at the beginning of the demonstration . It is therefore difficult to assess the effectiveness of methanogenesis with regard to xylene removal. In a previous study, performed with a sediment from a location other than the Seal Beach site, Edwards and Grbic-Galic [1994] found toluene and o-xylene to degrade under methanogenic conditions after lag times of 100–250 days. Other BTEX compounds did not degrade under these conditions.

In general, o-xylene appears to have been the second-most-readily degraded BTEX compound (next to toluene). The m+p-xylene isomers were relatively recalcitrant under sulfate-reducing conditions; under denitrifying conditions, m+p-xylene were removed more quickly than benzene and at about the same rate as ethylbenzene. The preferential degradation of o-xylene prior to m+p-xylene is somewhat surprising in the light of previous results [Haag et al., 1991; Edwards et al., 1992; Ball and Reinhard, 1996; Reinhard et al., 1997], although it might be expected under strictly methanogenic conditions [Edwards and Grbic-Galic, 1994].

5.1.5 Nitrate Concentration History: Nitrate was injected into zone 4 during the three augmentations. The first augmentation period ran from 9/14/97–10/16/97; the second augmentation ran from 5/24/98–6/23/98; the third augmentation period ran from 2 September

1998 through 14 October 1998. Figure 14 shows the concentration of nitrate injected into well I4, and the concentration measured at 4-B1-5, as functions of time. In all three injections, nitrate broke through at well bundle 4-B1 at a concentration lower than the injected concentration, presumably indicating microbial utilization of some of the nitrate between the injection well and the monitoring well. Bromide, a conservative tracer, broke through at 100% of its injected concentration (data not shown), indicating that the low nitrate breakthrough concentrations were not due to a poor hydraulic connection. Figure 14 also shows that, once the injection of nitrate ceased (indicating the onset of a no-flow stage in the test zone), the nitrate concentration at the monitoring well dropped rapidly. This drop in the nitrate concentration cannot be explained by ground water flow, because the injection/extraction wells were shut off during these periods, and the natural ground water flow is very slow. Once again, the most plausible explanation is that the drop in nitrate concentration was due to biological utilization of nitrate as an electron acceptor.

Figure 15 shows the nitrate breakthrough and decay at 4-B1-5 for the second augmentation only. We fit a first-order decay model to the measured nitrate concentrations assuming a travel time of 3 days between the injection well and 4-B1-5. The assumed 3-day travel time is consistent with the tracer data (not shown). The implied value of the first-order rate coefficient for nitrate utilization is 0.26/day. As can be seen from Figure 15, the results of the model fit are reasonable. The model used to estimate this rate coefficient is quite simplistic (no local dispersion accounted for, first-order kinetics rather than Monod kinetics), but might be useful to get a general idea of the rate of nitrate utilization. Fitting a first-order utilization model to the nitrate concentration data for the third augmentation produces an implied first-order rate coefficient of 0.1/day. The decrease in nitrate utilization rate between the second and third augmentations might indicate that (a) utilization is slower when nitrate is injected at higher concentrations, and/or (b) the rapidly-degradable substrates were consumed in the first two augmentations, such that the nitrate demand in the third augmentation was exerted by more slowly-degraded contaminants.

The rate of water injection during the flushing and augmentation stages is about 1.5 L/min in each well. Using this information, coupled with the measured nitrate concentrations in the zone 4 injection well, we were able to estimate that about 1.1 kg nitrate was added during the first augmentation, 3.3 kg nitrate in the second augmentation, and 9.3 kg nitrate in the third augmentation. Also, 2.2 kg nitrate was added to zone 2 during the third augmentation (see Table 4). Thus, the total amount of nitrate added during the three injections was about 15.9 kg. According to the stoichiometry shown in Equation (2), this would be enough to oxidize 3.3 kg of toluene (about 3.8 L, or 1.0 gal, if toluene were present as a pure non-aqueous phase) to carbon dioxide and water. In reality, much of the nitrate probably went to oxidize fuel hydrocarbons other than BTEX.

5.1.6 Sulfate Concentration History: Sulfate was injected into zones 2 and 4 during the three augmentations. In zone 2, sulfate was the only electron acceptor injected for the first two augmentations, but during the third augmentation, sulfate injection was preceded by nitrate injection. In zone 4, sulfate and nitrate were injected simultaneously for all three augmentations.

Figure 16 shows the concentrations of sulfate and nitrate injected into well I2, and the sulfate concentration measured at 2-B1-4, as functions of time. For all three augmentations, sulfate

broke through at the monitoring well at a concentration 75–80% of the injected concentration. This probably indicates biological utilization of some sulfate between the injection well and the monitoring well. Bromide, a conservative tracer, broke through at 100% of its injected concentration (data not shown), indicating that the apparent sulfate attenuation is not due to poor hydraulic connection between the injection and monitoring wells. Figure 16 also shows that, after each augmentation stage ended, indicating the onset of a no-flow stage, the sulfate concentration at 2-B1-4 dropped back down to almost zero. This is also evidence of biological utilization of sulfate. The drop in sulfate concentration cannot be explained by advection, because the injection and extraction wells were not running during the no-flow stages, and natural ground water flow is very slow: bromide persisted at nearly 100% of its injection concentration during the no-flow period. Therefore, biological utilization of sulfate is the most plausible explanation for the observed behavior.

Figure 17 shows the sulfate breakthrough and decay at 2-B1-4 for the second augmentation only. We fit a first-order decay model to the measured sulfate concentrations assuming a travel time of 2.5 days between the injection well and 2-B1-4. The assumed 2.5-day travel time is consistent with the tracer data (not shown). The implied value of the first-order rate coefficient for sulfate utilization is 0.1/day. As can be seen from Figure 17, the results of the model fit are reasonable. The model used to estimate this rate coefficient is quite simplistic (no local dispersion accounted for, first-order kinetics rather than Monod kinetics), but might be useful to get a general idea of the rate of sulfate utilization. Sulfate utilization is slightly slower than nitrate utilization for the same injected concentrations of sulfate and nitrate (cf. Figures 14 and 16).

Figure 16 also shows two other interesting features regarding the sulfate history in zone 2. The first of these interesting features is the large spike in observed sulfate concentration between 3/18/98 and 4/15/98. This was a rainy time period, and we believe the spike to be the result of rainwater infiltration from the surface. The flushing stage for the second augmentation began on 4/7/98, which is when the sulfate concentration very rapidly dropped from 180 mg/L back down to less than 20 mg/L.

The second interesting feature that can be seen in Figure 16 is an increase in the observed sulfate concentration at 2-B1-4 upon injection of nitrate into well I4 during the third augmentation. Figure 18 shows an interesting detail of the third augmentation. It appears that the introduction of nitrate was able to oxidize sulfide back to sulfate. It is presumed that sulfide had accumulated in zone 2 as a result of sulfate reduction from the first two augmentations. The ability of nitrate to oxidize sulfide to sulfate has been observed previously [Ball and Reinhard, 1996], and might be significant as a means of controlling sulfide inhibition.

Figure 19 shows the concentrations of sulfate and nitrate injected into well I4, and the nitrate and sulfate concentrations measured at 4-B1-5, as functions of time. The nitrate data at I4 and 4-B1-5 were also shown in Figure 14. In zone 4, sulfate broke through at the monitoring well at 100% of its injected concentration. This is in contrast to zone 2, where some sulfate utilization was observed between the injection well and the monitoring well. Also, in zone 4, when each augmentation ended, indicating the onset of a no-flow stage, the sulfate concentration at 4-B1-5 decayed at a much slower rate than was observed in zone 2. It appears that sulfate utilization is

slowed considerably by the presence of nitrate. This is not surprising, given that nitrate reduction is more energetically favorable than sulfate reduction for microorganisms [Borden, 1994]. It is unclear whether or not nitrate utilization and sulfate utilization are strictly sequential, i.e., whether sulfate utilization begins only after nitrate has been completely consumed. Figure 20 shows a detail of the second augmentation in zone 4. From Figure 20, it appears that some sulfate decay does occur while nitrate is still present, indicating that the two utilization processes can occur simultaneously and are not strictly sequential. However, the sulfate decay is rather slow, so this conclusion cannot be drawn definitively.

Figures 16 through 20 have shown the sulfate histories at monitoring well bundles 2-B1 and 4-B1, which are the well bundles closest to the respective injection wells (see Figure 4). At the well bundles further away from the injection well, the sulfate history does not correlate as strongly with the injected concentrations. Figure 21 shows the sulfate history at monitoring point 2-B2-4, which is located 4 m away from injection well I2. At well bundle 2-B2, the sulfate concentration appears to fluctuate almost randomly, and does not appear to depend on whether the system is being flushed or augmented. This might be an indication of a poor hydraulic connection between the injection well and well 2-B2. The results of a tracer test with bromide are inconclusive on this point; bromide injected into well I2 was seen to break through at nearly 100% at 2-B2-4 and 2-B2-6, but the implied travel time was about 3 weeks, which is much longer than would be expected based on the distance of 4 m between wells (Figure 22). Therefore, it is possible that the observed behavior at 2-B2-4 is due to natural fluctuations in the background sulfate concentration, and that 2-B2 is not hydraulically connected to injection well I2. However, even if this is the case, it is somewhat surprising that the background sulfate concentration would remain in the range 20–40 mg/L, given that there is BTEX contamination present at 2-B2. We would expect that the sulfate would be reduced biologically for BTEX oxidation, which would presumably result in background sulfate concentrations of less than 20 mg/L, as observed in well 2-B1. It is also possible that there is enough sulfide present at 2-B2 to inhibit the sulfate reduction; if 2-B2 is not hydraulically connected to I2, then this sulfide would not be removed during the flushing stages. This combination of factors could explain the continuously high sulfate concentration observed at 2-B2.

Based on injection flow rates of 1.5 L/min and the observed sulfate concentrations in the injection wells, we calculated that zone 2 received 1.3 kg sulfate in the first augmentation, 5.3 kg sulfate in the second augmentation, and 4.5 kg sulfate in the third augmentation, for a total of 11.1 kg. Zone 4 received 1.3 kg sulfate in the first augmentation, 5.3 kg sulfate in the second augmentation, and 6.9 kg sulfate in the third augmentation, for a total of 13.5 kg sulfate. The total amount of 24.6 kg sulfate added would, according to the stoichiometry shown in Equation (3), be enough to oxidize 5.2 kg of toluene (about 5.8 L, or 1.5 gal, if toluene were present as a pure non-aqueous phase) to carbon dioxide and water. In reality, much of the sulfate probably went to oxidize fuel hydrocarbons other than BTEX.

5.1.7 Methane Concentration History: Figure 23 shows the history of methane concentration in zones 2, 3, and 4. In all three zones, the initial methane concentration was greater than 5 mg/L, but dropped rapidly during the initial flushing and augmentation stages. During the first no-flow stage, the methane concentration in all three zones rose considerably, indicating the occurrence of

methanogenesis. The observed methanogenesis was weakest in zone 2. This is probably because zone 2 had the lowest total dissolved BTEX concentration; as shown by Equation (4), a lower BTEX concentration results in a lower produced methane concentration. The BTEX concentrations in zones 3 and 4 were comparable to each other, and so were the produced methane concentrations. Zone 3 exhibited somewhat more methanogenesis than zone 4, which might be an indication of a higher total concentration of fuel hydrocarbons. However, the lower methane concentrations in zone 4 might also be caused by the augmentation of nitrate and sulfate in that zone; nitrate and sulfate are both known to inhibit methanogenesis. In any event, the relatively high concentrations of methane produced in all three zones strongly suggests that fuel hydrocarbons were being degraded by fermentation and methanogenesis. According to the stoichiometry in Equation (4), an observed methane concentration of 5 mg/L would indicate the degradation of over 6 mg/L toluene. The high methane concentrations seem to indicate that other compounds in addition to BTEX were being degraded via methanogenesis.

5.1.8 Summary and Implications of Observed Concentration Histories: It appears that nitrate and sulfate were both utilized biologically for the oxidation of fuel hydrocarbons, including the BTEX compounds. This indicates that the enhancement of a contaminated aquifer via addition of electron acceptors can increase the rate of bioremediation of the aquifer. However, when nitrate and sulfate are not present, methanogenesis occurs, which should also lead to the bioremediation of the contaminated aquifer, albeit perhaps at a slower rate. Augmentation with electron acceptors appeared to increase the rate of degradation of ethylbenzene and the xylene isomers. However, augmentation did not appear to have much effect on the removal of benzene. Toluene was degraded under background conditions, i.e., even without the introduction of additional electron acceptors. The amount of nitrate and sulfate added during the three augmentations was enough to degrade about 8.5 kg BTEX. In reality, much of the sulfate and nitrate probably went to degrade fuel hydrocarbons other than BTEX. It is important to note, however, that during this project, we did not attempt to optimize the types and amounts of electron acceptors injected (e.g., no oxygen was added); rather, we were attempting to investigate anaerobic degradation under three different types of conditions.

5.2 Data Assessment

In general, we believe the reported data to be of high quality and to allow assessment of the demonstration's objectives. The Automated Sampling and Analysis Platform (ASAP) enabled us to compile a very large database of concentration histories at 105 different sampling point locations throughout the contaminated site. As a result, we have a very complete picture of how particular compounds responded to the treatment in time and in space.

Furthermore, the large database allows us to compare particular recorded measurements in order to provide an internal check on the consistency of the data. For instance, the BTEX concentrations were measured using gas chromatography with detection via photo-ionization (PID) and flame ionization (FID). The concentrations reported in this section are those that were measured via PID, which is believed to be more reliable for aromatic hydrocarbons; however, the FID measurements are available as a qualitative cross-check that the PID measurements are reasonable.

Also, the availability of seven sampling points spaced vertically at each monitoring well allows for another useful internal check on the data. We would not expect two different sampling points in the same well bundle to record exactly the same concentrations of a particular compound, but because there is not extreme physical heterogeneity at this site, we would expect the two sampling points to record similar trends. For example, Figure 24 shows the measured benzene concentration at two different vertical points in the same well bundle: points 2-B1-4 and 2-B1-6. Although the two monitoring points seldom produced identical concentration measurements for benzene, it is clear from Figure 24 that the two monitoring points were qualitatively in agreement with each other. This is precisely what we would expect from different points along the same vertical sampler.

As discussed in Section 5.1.6, above, this is not necessarily the case between different monitoring wells. For instance, Figure 21 showed that wells 2-B1 and 2-B2 produced very different measurements for sulfate concentration. However, we do not believe this to be an indication of poor data quality; rather, we believe that it indicates the spatial variability present at most field sites.

Despite our general confidence in the quality of the data, there are certain factors that confound the analysis. At any field site it is quite difficult to produce carefully controlled conditions. For instance, at the Seal Beach site, it is known that non-aqueous phase liquids (NAPLs) were present during this project. However, the exact amount and exact composition of the NAPL are unknown. Because of this, it is impossible to compute even a reasonable estimate for a mass balance on the BTEX compounds. The NAPL phase is believed to have acted as a source of BTEX throughout the duration of the demonstration, but the rate of BTEX dissolution from the NAPL phase into the aqueous phase is unknown. (Because gasoline is less dense than water, the NAPL tends to spread on top of the water table, such that BTEX concentrations in the saturated zone near the water table are quite high throughout the duration of the demonstration. In this report, we have chosen to focus on BTEX concentrations a few feet below the water table, where concentrations are low enough that the effects of the electron acceptors can be detected.) Other field processes also confound a quantitative analysis of the mass of BTEX degraded. Desorption of BTEX from aquifer solids into the aqueous phase, diffusion of BTEX from regions of high concentration into the treatment zones, and slow encroachment of native ground water can all lead to the introduction of additional BTEX into the aqueous phase of the treatment zones. Because of all these factors, it is impossible to use the data, regardless of their quality, to perform a quantitative analysis of BTEX degradation. A semi-quantitative analysis can be made on the basis of the electron acceptors added, because the composition of the injected water was carefully controlled via the above-ground water treatment system (Figures 5–7). Thus, a mass balance on the nitrate and/or sulfate injected is more reasonable than a mass balance on the actual fuel hydrocarbon contaminants.

5.3 Technology Comparison

At sites similar to the Seal Beach site, where fuel hydrocarbons contaminate the ground water, there are two primary alternatives to enhanced in situ bioremediation: pump-and-treat, and intrinsic bioremediation. Below, we compare each of these alternatives to enhanced in situ

bioremediation, using the results of this project as a guide. However, here it is important to recall that the technology implemented in this project was operated in a manner that differs from the recommended operation at a full-scale remediation site. For instance, because we were interested in evaluating three different types of anaerobic biodegradation, no oxygen was added to the injected feed water; at a full-scale implementation, oxygen could be added along with nitrate and sulfate in order to speed up the remediation.

Pump-and-treat remediation consists of extracting contaminated ground water from the site, treating the water above-ground to remove the contaminants of concern, and then either re-injecting the water into the aquifer or else disposing of it suitably. Essentially, the methodology used in this project is a pump-and-treat system with the added feature of augmenting the re-injected water with electron acceptors in order to stimulate in situ bioremediation. For a relatively minor modification, it is possible to derive great benefits in terms of the speed of aquifer remediation. Compare, for example, benzene to o-xylene. It was found (Section 5.1.1) that benzene was removed from the aquifer primarily via the extraction well, and subsequent adsorption onto activated carbon (Figures 5, 6). That is, benzene is removed primarily via pump-and-treat remediation. In contrast, o-xylene was rapidly degraded upon the addition of sulfate into zone 2 (Figure 12), and removal of o-xylene appears to be primarily via anaerobic biodegradation. Any contaminant mass that is degraded in situ does not need to be removed from the water in the above-ground treatment system. Thus, the in situ degradation of o-xylene extends the life of the activated carbon beds and shortens the amount of time that the extraction system must be run; both of these considerations indicate a savings in time and cost. Thus, as compared to a standard pump-and-treat remediation system, the demonstrated system has distinct advantages (shorter clean-up times, probably lower overall cost) and very few disadvantages (cost of electron acceptors, cost and maintenance of the chemical delivery system). The main question is whether or not the extra benefits are worth the additional cost of the electron acceptors and the injection system (Figure 7). This question will be considered in Section 6, below.

The other competing technology is intrinsic bioremediation. Intrinsic bioremediation consists of monitoring the site to ensure that no hazardous contaminants are reaching any receptors (e.g., drinking water wells, or, in this case, the Seal Beach National Wildlife Refuge), but does not employ injection of additional electron acceptors. Intrinsic bioremediation is therefore simpler and less expensive, because it does not require any injection wells, extraction wells, above-ground treatment system, or chemicals. However, there are some drawbacks to intrinsic bioremediation. It is likely to take much longer than enhanced bioremediation, especially if methanogenesis is much slower than sulfate reduction or nitrate reduction. This is especially true at a site like Seal Beach, where the very slow ground water flow limits the supply of electron acceptors and limits the removal of methane and inhibitory products. Methanogenesis is likely a more significant removal mechanism than either sulfate reduction or nitrate reduction at many fuel-contaminated ground water sites [Miller et al., 1995], and can lead to the generation of explosive methane gas. Furthermore, if a potential receptor is very close to the contaminated site, as in the case of Seal Beach, where the leaking tank was located very near the boundary of the wildlife refuge, intrinsic bioremediation might be insufficient to prevent the contamination from reaching the receptor. If a contaminated site is fairly isolated, and if the time for remediation is

not of major concern, and if all of the contaminants are known to degrade under the conditions naturally present, then intrinsic bioremediation is preferable to the enhanced bioremediation technology demonstrated here; however, under many circumstances, intrinsic bioremediation is probably inadequate.

5.4 Technology Evaluation

In Section 1.3 of this report, we stated that this project was intended to meet two broad objectives:

(1) Demonstration of a technology by which fuel hydrocarbons are removed from ground water via enhanced in situ anaerobic biodegradation
(2) Evaluation and quantification of the efficacy of three different anaerobic processes (methanogenic, sulfate-reducing, and combined sulfate- and nitrate-reducing).

Most of this report has been dedicated to a discussion of objective (1), the demonstration of the technology. However, objective (2) is also important, and in this section we address the quantification of the efficacy of the anaerobic processes.

If possible, the best way to quantify the efficacy of the three treatment processes would be to estimate the rate at which BTEX compounds are degraded under each of the three conditions. However, during the demonstration, it was possible to monitor only the aqueous BTEX concentrations, and not the amount sorbed or the amount present as residual NAPL. Therefore, it is impossible to estimate a rate at which the BTEX compounds were degraded.

However, as discussed above, it is possible to estimate the rate at which the electron acceptors nitrate and sulfate were utilized. Specifically, we found that nitrate was utilized with an apparent first-order rate constant of 0.1–0.26 day^{-1} when injected at concentrations of about 50–100 mg/L (see Figure 15). Sulfate was utilized with an apparent first-order rate constant of about 0.1 day^{-1} when injected (without nitrate) at a concentration of about 80 mg/L (Figure 17).

What is significant about these estimated rates is that they indicate that the injected electron acceptors would be nearly completely utilized during the augmentation and no-flow stages of a treatment cycle. This conclusion is supported by Figures 14–18, although Figures 19 and 20 suggest that sulfate might not be completely utilized when nitrate is present. If we assume that the electron acceptors are completely utilized during the augmentation an no-flow stages, then the efficacy of nitrate- and sulfate-reduction is essentially 100%, i.e., the rate of BTEX removal via anaerobic biodegradation is limited not by the kinetics of the biodegradation reaction, but rather by the rate at which nitrate and sulfate can be introduced into the contaminated region.

For Zone 2, we assume an injection rate of 1.5 L/min, an injection concentration of 80 mg/L sulfate, a 30-day augmentation period followed by a 30-day no-flow period, and the stoichiometry shown in Section 2.1.1. This results in the degradation of 1.1 kg of fuel hydrocarbons as a result of the sulfate augmentation.

For Zone 4, we assume an injection rate of 1.5 L/min, an injection concentration of 80 mg/L nitrate and 80 mg/L sulfate, a 30-day augmentation period followed by a 30-day no-flow period, and the stoichiometry shown in Section 2.1.1. This results in the degradation of 2.2 kg of fuel hydrocarbons as the result of sulfate and nitrate augmentation.

In Zone 3, where methanogenic conditions are established, it is impossible to quantify the efficacy of the anaerobic process without a method for measuring the sorbed BTEX concentrations and the amount present as residual NAPL.

6. Cost Assessment

6.1 Cost Performance

Tables 6, 7a, and 7b provide an assessment of the expected operational costs for the technology when implemented. The tables do not necessarily represent the actual cost of the particular demonstration described in this report; rather, they are a prediction of how much it should cost to implement this technology at a typical site. An example of typical site conditions is given below. These tables have been prepared in the format specified by the 1998 *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects*, which was prepared by the member agencies of the Federal Remediation Technologies Roundtable (FRTR). The tabulation specified by the 1998 Guide differs from that specified by the previous version of the Guide [FRTR, 1995].

As has been noted throughout this document, certain aspects of the demonstration project were performed under different operating conditions than would be expected at a full-scale implementation of this technology. Because the goal of this section is to provide information about the cost of a full-scale implementation of the technology, not the cost of the demonstration, it is important to specify the assumed parameters of the full-scale implementation. For the cost assessment, we make the following assumptions, which are all reasonable for a typical fuel-contaminated site:

- About 5,000 gallons of fuel leaked from an underground storage tank, contaminating the soil and shallow ground water. About 95% of the fuel (4750 gallons) was recovered via excavating the vadose zone down to the water table, or via some other removal mechanism. The remaining 250 gallons are present below the water table in three forms: as globules of non-aqueous phase liquid, dissolved in the ground water, and sorbed to aquifer solids.
- The spill has impacted a volume below the water table of about 3,000 m^3, of which approximately 2,000 m^3 is aquifer solids and 1,000 m^3 is contaminated ground water (based on a porosity of 0.33). The contaminated portion of the aquifer extends to about 3 m below the water table, and the areal extent of the contamination is about 1000 m^2, which is roughly one quarter of an acre.
- Five treatment zones are developed at the contaminated site, each consisting of an injection well and an extraction well. The injection rate and extraction rate in each zone are 4.6 L/min.
- A treatment cycle consists of a one-month flushing period, a one-month augmentation period, and a one-month no-flow period. Four treatment cycles are performed per year. Based on these parameters, about 200,000 L water are injected into each of the five treatment zones during the augmentation stage, for a total of 1,000,000 L injected during each augmentation stage.
- During the augmentation stages, nitrate is injected at 80 mg/L, sulfate at 80 mg/L, and oxygen at 9 mg/L.

- The reaction stoichiometries presented in Section 2 are valid. Therefore, the injection of 320 kg/year nitrate, 320 kg/year sulfate, and 36 kg/year oxygen degrades 145 kg/year fuel hydrocarbons (as toluene). This is equivalent to about 44 gallons/year.
- The above-ground treatment system for extracted water consists of granular activated carbon for hydrocarbon removal, followed by aeration for the removal of nitrogen gas (via stripping) and sulfide (via oxidation to sulfate). The treatment system operates eight months out of each year, i.e., during the flushing stages and during the augmentation stages, but not during the no-flow stages. Treated water is augmented with electron acceptors and is re-injected into the aquifer.
- The hydrocarbon concentration in extracted ground water averages 3 mg/L, and is effectively removed by the granular activated carbon. This is consistent with observations from the NWS Seal Beach demonstration. Therefore, about 24 kg/year hydrocarbons are removed via adsorption onto activated carbon, which is equivalent to about 7.2 gallons/year.
- The activated carbon system has an empty-bed volume of 230 L and an empty-bed contact time of 10 minutes. The system is loaded with 92 kg activated carbon (400 kg/m^3). During each treatment cycle, about 6 kg hydrocarbons are removed, such that the loading at the end of the treatment cycle is 65 g hydrocarbon per kg activated carbon. The activated carbon is replaced after each treatment cycle, i.e., four times annually.
- The overall hydrocarbon removal rate is 169 kg/year, equivalent to 51 gallons/year. About 85% of the removal is from in situ biodegradation, and about 15% is from activated carbon adsorption. The projected clean-up time is 4.9 years.

In addition, we assume that sampling and analysis are required on a monthly basis during the first year of operation, on a bi-monthly basis during the second and third years, and on a quarterly basis during the fourth and fifth years. This schedule is realistic in the sense that, as the remediation proceeds and clean-up is demonstrated, sampling and analysis can be performed on a less frequent basis. Thus, the operation and maintenance (O&M) costs for the project vary from year to year depending on the frequency of sampling and analysis. We assume that ten sampling locations are monitored over time. Finally, we assume that O&M costs are subject to an annual increase in price of 5% due to inflation, but that the present value of future costs is represented by an 8% annual discount rate.

Under these conditions, Table 6 summarizes the anticipated capital costs, while Tables 7a and 7b summarize the present value of the operating and maintenance (O&M) costs. The estimated capital cost is $470,000. The estimated present value of the O&M costs is $615,000 over 5 years. The total present value of the clean-up costs is $1,085,000, or $4,340 per gallon of fuel hydrocarbon recovered.

These cost estimates are based on an assumed set of conditions, as described above. The assumed conditions are reasonable, and are representative of many of the sites at which this technology might be applied. However, actual conditions can vary widely from site to site, and the cost estimates provided here should not be considered to apply exactly to all sites. For instance, if the contaminated area is larger than that assumed here, then more than 5 injection-extraction well pairs might be required, and more than ten monitoring wells might be required. This would increase both the capital cost (more wells needed, higher mobilization costs, etc.) and the O&M

costs (more samples requiring analysis, more rapid activated carbon use, etc.). Of course, a larger contaminated area would also mean that competing technologies would probably be more expensive, as well, but the costs might not increase in equal proportions for all technologies under consideration. Therefore, even though the cost estimates in this report are believed to be quite reasonable and accurate for the representative site conditions considered, each contaminated site should be considered individually when a remediation technology is being selected.

6.2 Cost Comparisons to Conventional and Other Technologies

As discussed in Section 5.3, above, the two most common alternatives to the technology described here are (1) pump-and-treat, and (2) intrinsic bioremediation. Below, we estimate the clean-up times and the costs if the conventional pump-and-treat method were applied to the "typical" spill described in Section 6.1, above. We also consider the conditions under which intrinsic bioremediation might or might not be preferable to the Enhanced In Situ Anaerobic Bioremediation method. Finally, we consider when enhanced aerobic biodegradation (e.g., via air sparging) might be a viable alternative.

Table 6: Capital Cost for Enhanced In Situ Bioremediation Technology

Capital Cost Element	Cost	Sub-Cost
Site Characterization:		
Hydrogeologic characterization:	$100,000	
Wells for estimating hydraulic head and gradient:		$60,000
Pump tests to estimate hydraulic conductivity:		$20,000
Cores and core analysis to estimate hydraulic conductivity:		$20,000
Microcosm studies to test biological activity:	$10,000	
Technology mobilization, set-up, and demobilization:		
Transportation/delivery of equipment, facilities, and personnel:	$20,000	
Set-up of temporary facilities (e.g., trailer) and utilities:	$20,000	
Demobilization:	$10,000	
Planning and preparation:		
Engineering design and modeling:	$50,000	
Permits and licenses, including air emission and water discharge:	$20,000	
License fees associated with use of a technology:	$0	
Regulatory interaction:	$5,000	
Written plans:	$35,000	
Work plans:		$10,000
Sampling and analysis plans:		$10,000
Health and safety plans:		$5,000
Community relations plans:		$5,000
Site management plans:		$5,000
Site work:		
Establish physical infrastructure for technology application:	$15,000	
Activities necessary to restore site to pre-remediation conditions:	$15,000	
Activities necessary to meet specifications of site restoration plan:	$15,000	
Preparing specific site of the technology:	$15,000	
Clearing and grubbing:		$5,000
Earthwork:		$5,000
Construction of utilities, culverts, treatment pads, foundations, etc.:		$5,000
Installation of treatment system (equipment and appurtenances):		
Extraction wells (5 wells, $5000 each):	$25,000	
Injection wells for augmentation (5 wells, $5000 each):	$25,000	
Monitoring wells (10 multi-level samplers, $5000 each):	$50,000	
Above-ground water treatment system:	$10,000	
Activated Carbon column (1 m length, 0.5 m diameter):		$2,000
Trickling Filter for aeration:		$6,000
Chemical Injection System:		$2,000
Startup and testing:		
Establishment of operating conditions:	$5,000	
Shakedown:	$5,000	
Training of O&M personnel:	$5,000	
Other capital costs:		
Data processing and computer equipment:	$5,000	
Safety equipment:	$5,000	
Vehicles:	$5,000	
Total Capital Cost:	$470,000	

Table 7a: Annual Operating and Maintenance (O&M) Costs for Technology

O&M Cost Element	Cost	Sub-Cost
Labor:		
Maintenance of technology and associated equipment:	$25,000	
Labor supervision:	$5,000	
Payroll expenses:	$5,000	
Materials:		
Consumable supplies:	$5,000	
Activated carbon (replaced quarterly; includes disposal):		$5,000
Process materials:	$0	
Bulk chemicals:	$13,000	
Nitrate (320 kg/year):		$7,000
Sulfate (320 kg/year):		$6,000
Raw materials:	$0	
Utilities and fuel		
Fuel:	$500	
Electricity: (primarily for running pumps)	$1,000	
Natural gas:	$0	
Water:	$500	
Equipment ownership, rental, or lease:	$0	
Performance testing and analysis:		
Monitoring, sampling, analysis ($1000 per well per round):	see Table 7b	
Other O&M Costs:		
Maintenance and repair of office/administrative equipment:	$5,000	
Health and safety costs:	$5,000	
Personal protective equipment:		$2,000
Monitoring of personnel for health and safety:		$3,000
Total Annual O&M Costs (not including monitoring):	$65,000	
Total Annual O&M Costs (including monitoring):	see Table 7b	

Table 7b: Present Value of O&M Costs, Including Monitoring
Enhanced In Situ Anaerobic Bioremediation Method

Year	Sampling Frequency	Monitoring Cost (Unadjusted)	Total O&M Cost (Unadjusted)	O&M Cost (with inflation)	O&M Cost (present value)
1	Monthly	$120,000	$185,000	$185,000	$185,000
2	Bi-Monthly	$60,000	$125,000	$131,250	$121,528
3	Bi-Monthly	$60,000	$125,000	$137,813	$118,152
4	Quarterly	$40,000	$105,000	$121,551	$96,491
5	Quarterly	$40,000	$105,000	$127,628	$93,811
Total O&M Cost, Present Value					$615,000

Notes: Sampling frequency is assumed to follow the schedule above
Costs based on assumption of ten (10) monitoring wells and cost of $1000 per well per round of sampling/analysis
Inflation rate assumed 5% annually, discount rate assumed 8%
Clean-up time for this method estimated to be 5 years
Other site characteristics described in Section 6.1

6.2.1 Comparison to Pump-and-Treat (Conventional Clean-up)

Our cost estimate for the pump-and-treat remediation is based upon the following assumptions:

- Site conditions are the same as those described in Section 6.1, above, but with the following differences.
- Five extraction wells are installed, each with a flow rate of 4.6 L/min. This is the same specification that was made in the cost estimate for the proposed technology in Section 6.1, above. The wells are operated continuously, such that a total of 12,100,000 L are extracted in one year.
- Extracted water is treated with granular activated carbon for hydrocarbon removal. Air stripping might also be possible, but to facilitate comparison with the proposed technology as described in Section 6.1, we assume that activated carbon is suitable.
- The hydrocarbon concentration in extracted ground water averages 3 mg/L, and is effectively removed by the granular activated carbon. This is consistent with observations from the NWS Seal Beach demonstration. Therefore, about 36 kg/year hydrocarbons are removed via adsorption onto activated carbon, which is equivalent to about 11 gallons/year.
- The activated carbon system has an empty-bed volume of 230 L and an empty-bed contact time of 10 minutes. The system is loaded with 92 kg activated carbon (400 kg/m^3). The carbon is replaced every two months, such that the hydrocarbon loading just before replacement is about 65 g hydrocarbon per kg of activated carbon.

- Some in situ biological removal is expected, either aerobic or via methanogenesis, even without addition of sulfate or nitrate as electron acceptors. We assume that about 20 kg/year are degraded biologically.
- The total hydrocarbon removal rate is 56 kg/year, which is equivalent to about 17 gallons/year. The total clean-up time is 14.7 years.
- There are some costs that are expected to be lower for the pump-and-treat technology than for the proposed enhanced in situ bioremediation technology. Specifically,
- Assuming that the treated water is discharged, no injection wells are required for re-injection of treated water.
- Because pump-and-treat is an established technology, fewer samples are required during the monitoring program. We assume seven monitoring locations for the pump-and-treat method, as opposed to ten monitoring locations for the enhanced in situ bioremediation method.
- The above-ground treatment system does not require aeration or chemical injection.
- Because less equipment is required, design and delivery costs are somewhat lower.
- No sulfate or nitrate is required.

In addition, we assume that sampling and analysis are required on a bi-monthly basis during the first 9 years of operation, and on a quarterly basis during the final 6 years. This schedule is realistic in the sense that, as the remediation proceeds and clean-up is demonstrated, sampling and analysis can be performed on a less frequent basis. We assume that 7 sampling locations are monitored (as opposed to 10 locations for the enhanced in situ bioremediation scheme described above). As before, we assume that O&M costs are subject to an annual increase in price of 5% due to inflation, but that the present value of future costs is represented by an 8% annual discount rate.

Under these conditions, Table 8 summarizes the anticipated capital costs, while Tables 9a and 9b summarize the present value of the O&M costs. The estimated capital cost is $397,000. The estimated present value of the O&M costs is $1,143,000 over 15 years. The total present value of the clean-up costs is $1,540,000, or $6,160 per gallon of fuel hydrocarbon recovered.

Based on this analysis, the proposed technology, enhanced in situ bioremediation, is preferable to conventional pump-and-treat remediation. Although there are some additional costs associated with implementing a relatively new technology, the overall cost is lower, and the associated clean-up time is much shorter (about 5 years instead of about 15 years). However, it is important to note that the extent of biodegradation for the conventional pump-and-treat remediation is extremely uncertain. We have assumed 20 kg/year biodegradation, but if the actual rate is much faster or much slower, then the cost for the pump-and-treat remediation could be affected significantly. Table 9b gives an indication how the estimated cost could be adjusted for shorter or longer clean-up times.

Table 8: Capital Cost for Conventional Pump-and-Treat Technology

Capital Cost Element	Cost	Sub-Cost
Site Characterization:		
Hydrogeologic characterization:	$100,000	
Wells for estimating hydraulic head and gradient:		$60,000
Pump tests to estimate hydraulic conductivity:		$20,000
Cores and core analysis to estimate hydraulic conductivity:		$20,000
Technology mobilization, set-up, and demobilization:		
Transportation/delivery of equipment, facilities, and personnel:	$15,000	
Set-up of temporary facilities (e.g., trailer) and utilities:	$20,000	
Demobilization:	$10,000	
Planning and preparation:		
Engineering design and modeling:	$40,000	
Permits and licenses, including air emission and water discharge:	$20,000	
License fees associated with use of a technology:	$0	
Regulatory interaction:	$5,000	
Written plans:	$35,000	
Work plans:		$10,000
Sampling and analysis plans:		$10,000
Health and safety plans:		$5,000
Community relations plans:		$5,000
Site management plans:		$5,000
Site work:		
Establish physical infrastructure for technology application:	$15,000	
Activities necessary to restore site to pre-remediation conditions:	$15,000	
Activities necessary to meet specifications of site restoration plan:	$15,000	
Preparing specific site of the technology:	$15,000	
Clearing and grubbing:		$5,000
Earthwork:		$5,000
Construction of utilities, culverts, treatment pads, foundations, etc.:		$5,000
Installation of treatment system (equipment and appurtenances):		
Extraction wells (5 wells, $5000 each):	$25,000	
Monitoring wells (7 multi-level samplers, $5000 each):	$35,000	
Above-ground water treatment system:	$2,000	
Activated Carbon column (1 m length, 0.5 m diameter):		$2,000
Startup and testing:		
Establishment of operating conditions:	$5,000	
Shakedown:	$5,000	
Training of O&M personnel:	$5,000	
Other capital costs:		
Data processing and computer equipment:	$5,000	
Safety equipment:	$5,000	
Vehicles:	$5,000	
Total Capital Cost:	$397,000	

Table 9a: Annual (O&M) Costs for Conventional Pump-and-Treat Technology

O&M Cost Element	Cost	Sub-Cost
Labor:		
Maintenance of technology and associated equipment:	$25,000	
Labor supervision:	$5,000	
Payroll expenses:	$5,000	
Materials:		
Consumable supplies:	$7,500	
Activated carbon (replaced quarterly; includes disposal):		$7,500
Process materials:	$0	
Raw materials:	$0	
Utilities and fuel		
Fuel:	$500	
Electricity: (primarily for running pumps)	$1,500	
Natural gas:	$0	
Water:	$500	
Equipment ownership, rental, or lease:	$0	
Performance testing and analysis:		
Monitoring, sampling, analysis ($7,000 each round):	see Table 9b	
Other O&M Costs:		
Maintenance and repair of office/administrative equipment:	$5,000	
Health and safety costs:	$5,000	
Personal protective equipment:		$2,000
Monitoring of personnel for health and safety:		$3,000
Total Annual O&M Costs (not including monitoring):	$55,000	
Total Annual O&M Costs (including monitoring):	see Table 9b	

Table 9b: Present Value of O&M Costs, Including Monitoring
Conventional Pump-and-Treat Method

Year	Sampling Frequency	Sampling Cost (Unadjusted)	Total O&M Cost (Unadjusted)	O&M Cost (with inflation)	O&M Cost (present value)
1	Bi-Monthly	$42,000	$97,000	$97,000	$97,000
2	Bi-Monthly	$42,000	$97,000	$101,850	$94,306
3	Bi-Monthly	$42,000	$97,000	$106,943	$91,686
4	Bi-Monthly	$42,000	$97,000	$112,290	$89,139
5	Bi-Monthly	$42,000	$97,000	$117,904	$86,663
6	Bi-Monthly	$42,000	$97,000	$123,799	$84,256
7	Bi-Monthly	$42,000	$97,000	$129,989	$81,915
8	Bi-Monthly	$42,000	$97,000	$136,489	$79,640
9	Bi-Monthly	$42,000	$97,000	$143,313	$77,428
10	Quarterly	$28,000	$93,000	$128,760	$64,412
11	Quarterly	$28,000	$93,000	$135,198	$62,623
12	Quarterly	$28,000	$93,000	$141,958	$60,883
13	Quarterly	$28,000	$93,000	$149,056	$59,192
14	Quarterly	$28,000	$93,000	$156,509	$57,548
15	Quarterly	$28,000	$93,000	$164,334	$55,949
Total O&M Cost, Present Value					$1,143,000

Notes: Sampling frequency is assumed to follow the schedule above
Costs based on assumption of seven (7) monitoring wells and cost of $1000 per well per round of sampling/analysis
Inflation rate assumed 5% annually, discount rate assumed 8%
Clean-up time for this method estimated to be 15 years
Other site characteristics described in Sections 6.1 and 6.2.1

6.2.2 Comparison to Intrinsic Bioremediation. When intrinsic bioremediation is technically feasible, it is almost certain to cost less than the proposed enhanced bioremediation technology. Intrinsic bioremediation does not require the installation of injection wells, extraction wells, or above-ground water treatment equipment. The primary cost for intrinsic bioremediation is the cost of monitoring, sampling, and analysis. Although this cost can be substantial, particularly if the remediation takes several years, the overall cost of intrinsic bioremediation is low in comparison to the other treatment technologies considered here.

Therefore, the determining factor as to whether or not intrinsic bioremediation is preferable to enhanced bioremediation is the expected effectiveness of intrinsic biological processes. The following issues need to be considered:

1) At sites like Seal Beach, where the very slow ground water flow limits the supply of electron acceptors and limits the removal of methane and inhibitory products, intrinsic bioremediation might be extremely slow.
2) During intrinsic bioremediation, methanogenesis is often the most significant biological removal process [Miller et al., 1995], which can lead to the build-up of explosive methane gas.
3) If the contaminated site is located close to potential receptors, as in the case of Seal Beach, where the leaking tank was very near the boundary of the wildlife refuge, intrinsic bioremediation might be insufficient to prevent the contamination from reaching the receptor.

Therefore, although intrinsic bioremediation is almost certain to be less expensive than the enhanced bioremediation demonstrated here, there are many circumstances in which intrinsic bioremediation is unsuitable. In such cases, enhanced in situ bioremediation is likely to be a viable alternative.

6.2.3 Comparison to Enhanced Aerobic Biodegradation. Another alternative method to that demonstrated in this project is Enhanced Aerobic Biodegradation. Enhanced Aerobic Biodegradation would consist of the introduction of oxygen into the aquifer rather than alternate electron acceptors such as sulfate or nitrate, in an effort to stimulate aerobic organisms to oxidize BTEX to carbon dioxide and water. Aerobic biodegradation of BTEX compounds is generally faster than anaerobic degradation, and can in some cases be considerably faster, particularly for benzene. Therefore, if oxygen can be introduced into the aquifer effectively and inexpensively, then Enhanced Aerobic Biodegradation would probably be preferable to Enhanced Anaerobic Biodegradation.

However, delivery of oxygen into a contaminated aquifer can be difficult and/or expensive. Methods include:

1) Injecting water saturated with dissolved oxygen gas
2) Injecting water with some concentration of peroxide, which quickly reacts to produce molecular oxygen
3) Air sparging, i.e., the introduction of oxygen gas bubbles at the bottom of the contaminated region, which allows the bubbles to flow upwards through the contaminated region, delivering oxygen to the bacteria while simultaneously stripping volatile contaminants out of the water
4) Placing oxygen-releasing compounds (ORCs) in situ to provide a continuous supply of oxygen.

However, each of these techniques has its own limitations. For instance,

1) the solubility of oxygen in water is low, so that nitrate and sulfate can be introduced at much higher concentrations than oxygen.
2) Peroxide is a very reactive, unstable compound, which reacts unselectively with aquifer materials, e.g., peroxide can oxidize ferrous iron, Fe^{2+}, to ferric iron, Fe^{3+}. This consumes the peroxide and can result in precipitation of ferric compounds.
3) Air sparging must be used in conjunction with a soil vapor extraction (SVE) system, which makes it expensive, and the delivery of oxygen to the necessary locations via air sparging is unreliable and can be limited by the rate of oxygen diffusion.
4) Oxygen-releasing compounds (ORCs) might be the most promising of these oxygen delivery methods, but the technology is still developing. In some cases use of ORCs has been found to alter aquifer pH, or to decrease the permeability of the aquifer matrix, presumably due to precipitation caused by oxidation of minerals in the matrix. Also, ORCs might deliver oxygen to only a relatively small vicinity around the ORC compound, while other regions of the aquifer remain anaerobic.

There may also be other limitations to these methods not considered here. By contrast, delivery of nitrate and sulfate at relatively high concentrations is a relatively simple process.

Finally, we note here that the Enhanced In Situ Bioremediation technology demonstrated in this project is, in fact, a hybrid aerobic/anaerobic treatment method. Because oxygen is consumed rapidly, the anaerobic processes are of extreme importance, and have been emphasized in the demonstration of this technology. However, as noted elsewhere in this report, a full-scale implementation of this project would include the introduction of oxygen into the aquifer as well as the introduction of nitrate and sulfate.

7. Regulatory Issues: Approach to Regulatory Compliance and Acceptance

Extracting and re-injecting ground water requires permission from the appropriate regulatory agencies. As discussed in Section 1.4, above, there are three main regulatory issues with regard to the implementation of the technology described in this report:

(1) Nitrate, which has a drinking water maximum contaminant level (MCL) of 45 mg/L, is injected into the ground water as an electron acceptor. In order for the technology to operate at maximum efficiency, nitrate should be injected at a concentration higher than its MCL. Regulatory approval is required for injection of nitrate at high concentrations.

(2) Contaminated ground water is extracted, treated, augmented with electron acceptors, and then re-injected into the aquifer. The re-injection of treated ground water requires regulatory approval.

(3) It must be satisfactorily demonstrated that sufficient hydraulic control is established, so that the plume can be contained if any problem arises during implementation of the remediation technology.

For the demonstration at NWS Seal Beach, we first injected nitrate at low concentrations and monitored the subsequent biological utilization of nitrate. When we had demonstrated that nitrate was biologically degraded very rapidly, regulators were amenable to the injection of higher concentrations of nitrate.

We found regulators to be concerned with the re-injection of treated ground water into the aquifer. Demonstration of hydraulic control of the site and formulation of appropriate contingency plans are helpful aides in obtaining regulatory approval for re-injection.

8. Technology Implementation

8.1 Department of Defense (DOD) Need

In April 1997, the United States Environmental Protection Agency (EPA) published a report that included a survey of the demand for remediation of DOD sites [U.S. EPA, 1997a]. Among the relevant findings of that report were the following:

- Based on 1995 site data, an estimated 8,336 DOD sites would require clean-up.
- Based on 1994 site data, 3,212 sites had identified both the types of contaminated media (ground water, soil, surface water, and/or sediment) and the types of contaminants present (volatile organic compounds, semivolatile organic compounds, metals, fuels, explosives, etc.). Of these 3,212 sites,
    - 2,290 (71%) had contaminated ground water.
    - 2,093 were contaminated with VOCs and 712 were contaminated with fuels. Benzene, toluene, ethylbenzene, and xylene (BTEX) could be categorized in either the VOCs category or the fuels category.
    - 22% were explicitly recognized as containing BTEX contamination. However, the actual percentage of sites with BTEX contamination might be higher if some BTEX sites were classified in the more general VOCs category (44% of sites were identified with non-halogenated VOCs).

Assuming that 71% of all DOD sites have contaminated ground water, and also making a conservative assumption that 22% of ground water sites are contaminated with fuel hydrocarbons, then we would expect fuel contamination at 1,302 of the 8,336 sites identified in 1995. This number is probably a conservative estimate, and the actual number of DOD sites where ground water is contaminated with fuel hydrocarbons might be several thousand. Based on this assessment, we consider the technology described in this report to be of extreme interest to DOD. Not all sites will have conditions amenable to the implementation of this technology, but many sites will.

8.2 Transition and Technology Transfer

The major impediment to full-scale application of this technology is the fact that, despite the significant progress made in this project, questions still remain regarding the efficacy of anaerobic remediation of fuel hydrocarbons under different geochemical conditions. The hydraulic components of the technology, although highly dependent upon specific site conditions, are well established and well understood. This is also true for the above-ground water treatment of the extracted water. The primary difficulty in applying this technology to a full-scale site is the determination of what electron acceptors should be injected, and at what concentrations. Among the BTEX compounds, only toluene has been observed to degrade rapidly under general anaerobic conditions. Biodegradation of the other compounds appears to be highly dependent upon the terminal electron acceptor(s) present and also upon other site-specific conditions that are much more difficult to identify.

We recommend two ways in which these difficulties can be mitigated:

(1) Further exploration, under carefully controlled laboratory conditions as well as actual field conditions, to better determine what specific factors control microorganisms' ability to degrade BTEX and other fuel hydrocarbons
(2) Whenever this technology is implemented full-scale, installation at the contaminated aquifer should be preceded by laboratory experiments with the aquifer material in order to determine how fast particular contaminants degrade under different geochemical conditions.

Active research on anaerobic biodegradation is underway at many universities and government laboratories, which should improve our understanding and ability to apply this technology in the coming years.

A related issue is whether or not this technology is preferable to monitored intrinsic bioremediation, which is currently favored by many industries. Monitored intrinsic bioremediation alleviates the uncertainty over electron acceptor selection by relying completely on whatever conditions are naturally present. This also makes monitored intrinsic bioremediation less expensive than enhanced bioremediation. The choice between the two technologies is largely one of economics; enhanced bioremediation is expected to lead to shorter clean-up times, especially at sites where sulfate reduction and/or denitrification are known to accelerate biodegradation.

This technology should be readily acceptable by regulatory agencies (see also Section 1.4 and Section 7). Although we did not have an industrial partner during this demonstration, we expect the technology to be rapidly accepted by industry. The equipment employed is readily available commercially, and is commonly installed in other types of treatment systems. Ground water contamination from leaking underground storage tanks is a very large industrial problem [National Research Council, 1994], especially with regard to fuel hydrocarbons. Therefore, we anticipate industry to be extremely interested in the continued development of this technology.

9. Lessons Learned

Below, we summarize some of the most important scientific and technical findings from this demonstration project. These findings should be useful to those who are planning a demonstration of enhanced anaerobic in situ bioremediation, or those who are attempting to implement this technology at a full-scale remediation site.

- Nitrate and sulfate can be utilized biologically as electron acceptors during the in situ anaerobic oxidation of fuel hydrocarbons (including BTEX compounds) in contaminated ground water. Therefore, bioremediation of contaminated ground water can be enhanced (accelerated) via the introduction of nitrate and/or sulfate into the contaminated region. However, sulfate reduction, denitrification, and fermentation/methanogenesis can all occur naturally under unaugmented conditions. Therefore, the benefits of accelerated degradation via nitrate/sulfate augmentation must be assessed vis-a-vis natural attenuation (intrinsic bioremediation), which is less costly to implement.
- Ground water contaminated from gasoline contains not only BTEX compounds, but many other gasoline components as well. At the Seal Beach site, much of the injected nitrate and sulfate was utilized by bacteria to degrade non-BTEX hydrocarbons. This makes it difficult to predict the amount of electron acceptor(s) that will be needed for complete BTEX removal.
- At the Seal Beach site, nitrate utilization was fast. Most or all of the injected nitrate was consumed within 30 days after injection ceased for the third augmentation, and even faster for the first and second augmentations. Sulfate utilization was also relatively fast in the region where sulfate was the only electron acceptor injected. In the region where both sulfate and nitrate were injected, the sulfate utilization was much slower.
- Injection of nitrate at very high concentrations (greater than 100 mg/L) might lead to the formation of nitrogen gas bubbles, which could alter the hydraulic character of the aquifer.
- Methanogenesis was observed in all three treatment zones during the demonstration, but was most apparent in the zone where neither nitrate nor sulfate was added. In two of the zones, several mg/L methane were generated (5–6 mg/L in zone 3, and 3–5 mg/L in zone 4), which would correspond to the degradation of several mg/L fuel hydrocarbons. However, it did not appear that benzene was effectively removed via methanogenesis.
- The removal rate and the removal sequence for BTEX compounds depends on a number of factors, including the terminal electron acceptor. Toluene concentrations were very low even at the onset of the demonstration, consistent with previously-observed preferential toluene degradation under sulfate-reducing, denitrifying, and methanogenic conditions. Augmentation with nitrate was effective for the removal of all BTEX compounds except benzene. Augmentation with sulfate accelerated the removal of xylenes, particularly o-xylene, but not the other BTEX compounds.
- Benzene was effectively removed via flushing, in part because it does not sorb strongly to aquifer materials. However, benzene biodegradation was slow if it occurred at all. Some previous studies have shown that benzene biodegradation occurs only when no other BTEX compounds are present, indicating a preferential removal sequence.

- During periods when the injection and extraction wells were not operated, a rebound in the BTEX concentrations was observed, especially for benzene. This probably indicates the presence of a residual non-aqueous liquid (NAPL) phase, but it might also indicate the desorption of BTEX compounds from aquifer solids, the diffusion of BTEX from highly contaminated areas that are not effectively flushed, and/or slow encroachment of highly contaminated ground water.
- Many of the design parameters for this system depend on site-specific contamination and hydrogeologic conditions. Some of these design parameters include: the number and location of extraction and injection wells; the injection and extraction flow rates; the method of above-ground treatment for extracted water; the choice of electron acceptors injected; the concentrations of electron acceptors injected; and the duration of flushing, augmentation, and no-flow periods.

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Figure 1. Location of the Naval Weapons Station, Seal Beach and the Seal Beach National Wildlife Refuge.

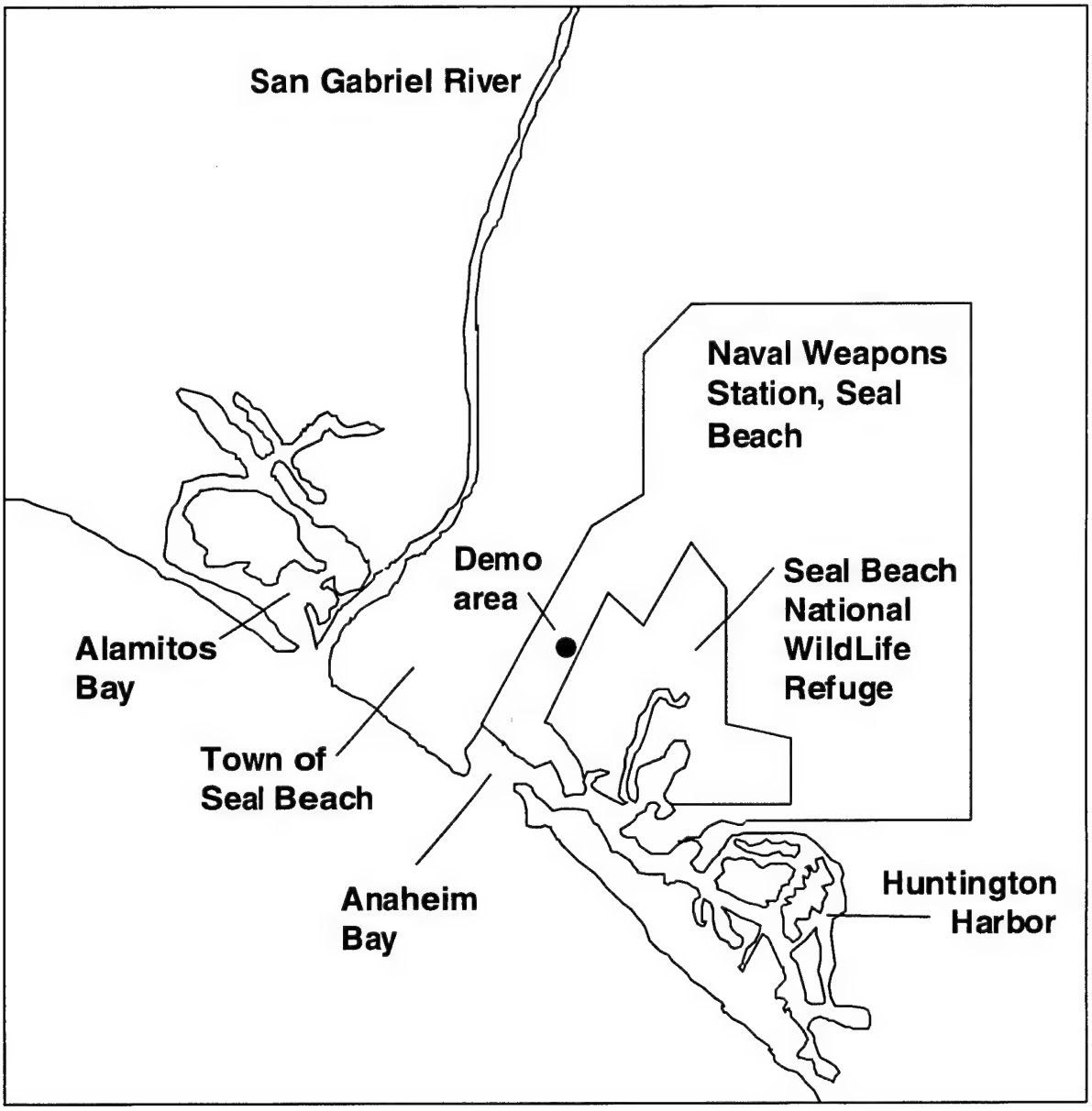

Figure 2. Detailed location of the Naval Weapons Station, Seal Beach and the Seal Beach National Wildlife Refuge.

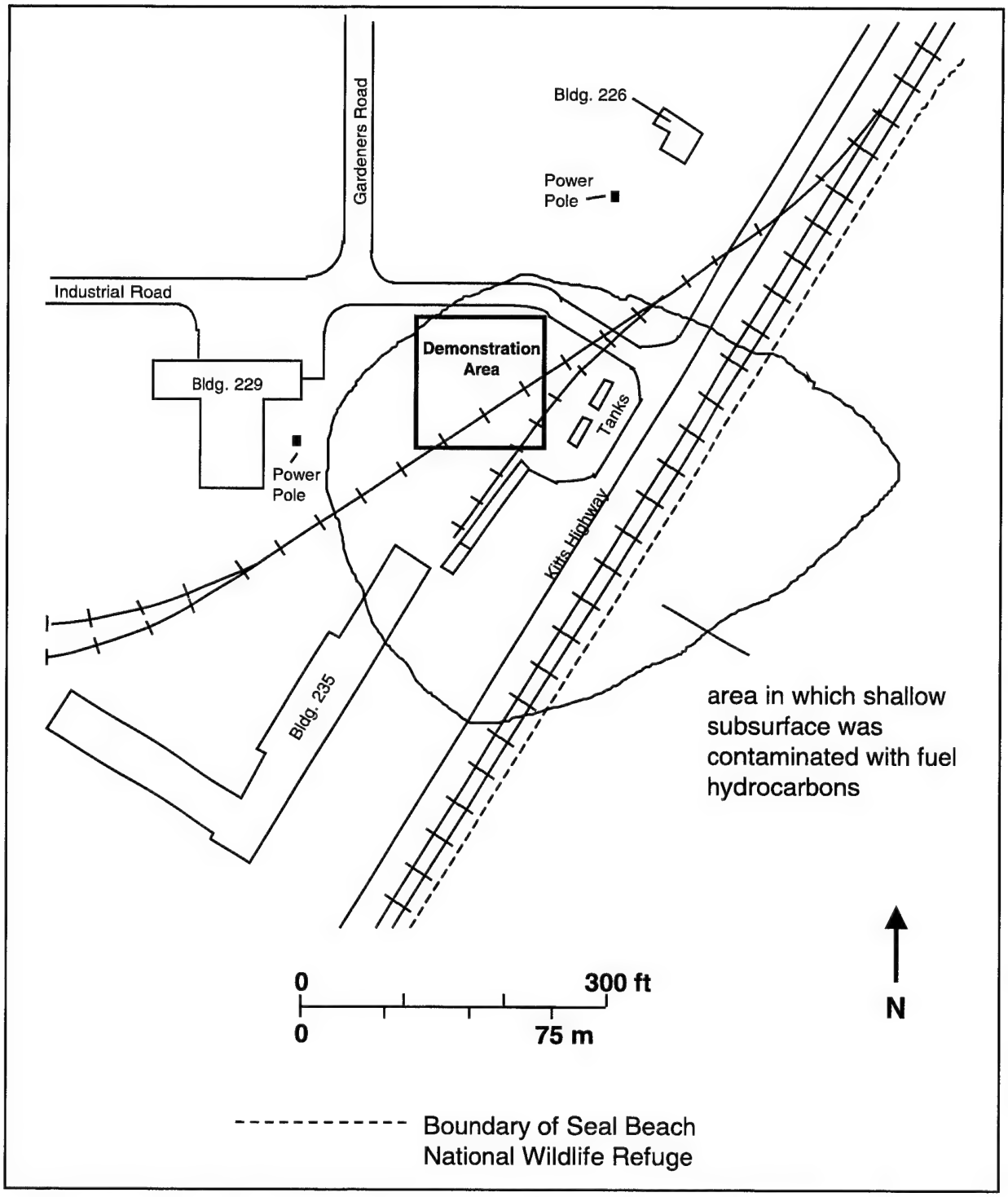

Figure 3. Plan view of the region of ground water contamination and the demonstration area.

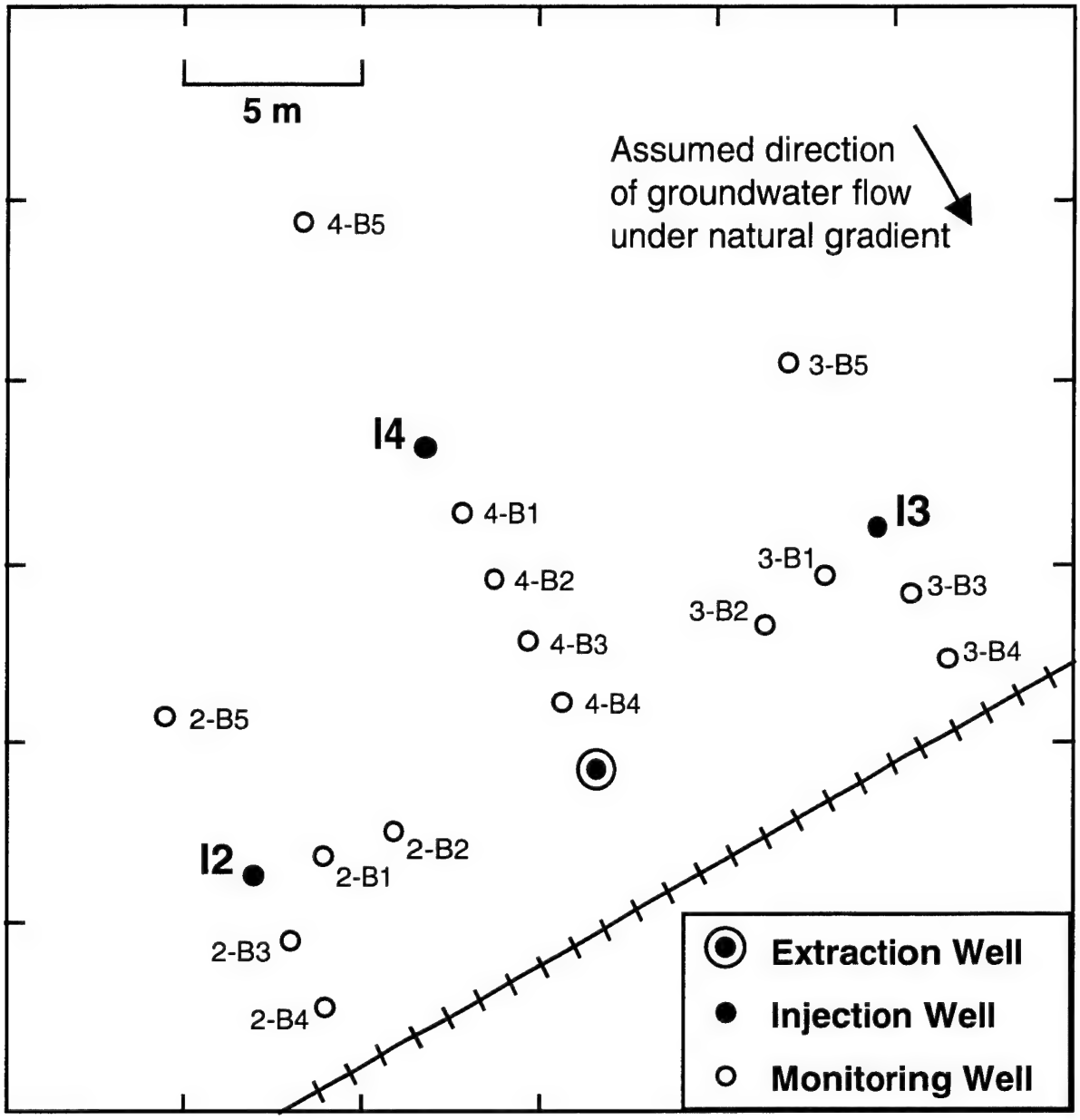

Figure 4. Plan view of the injection wells, extraction wells, and monitoring wells in the demonstration area. Zone 2 is amended with sulfate, Zone 3 is methanogenic (unamended), and Zone 4 is amended with nitrate and sulfate

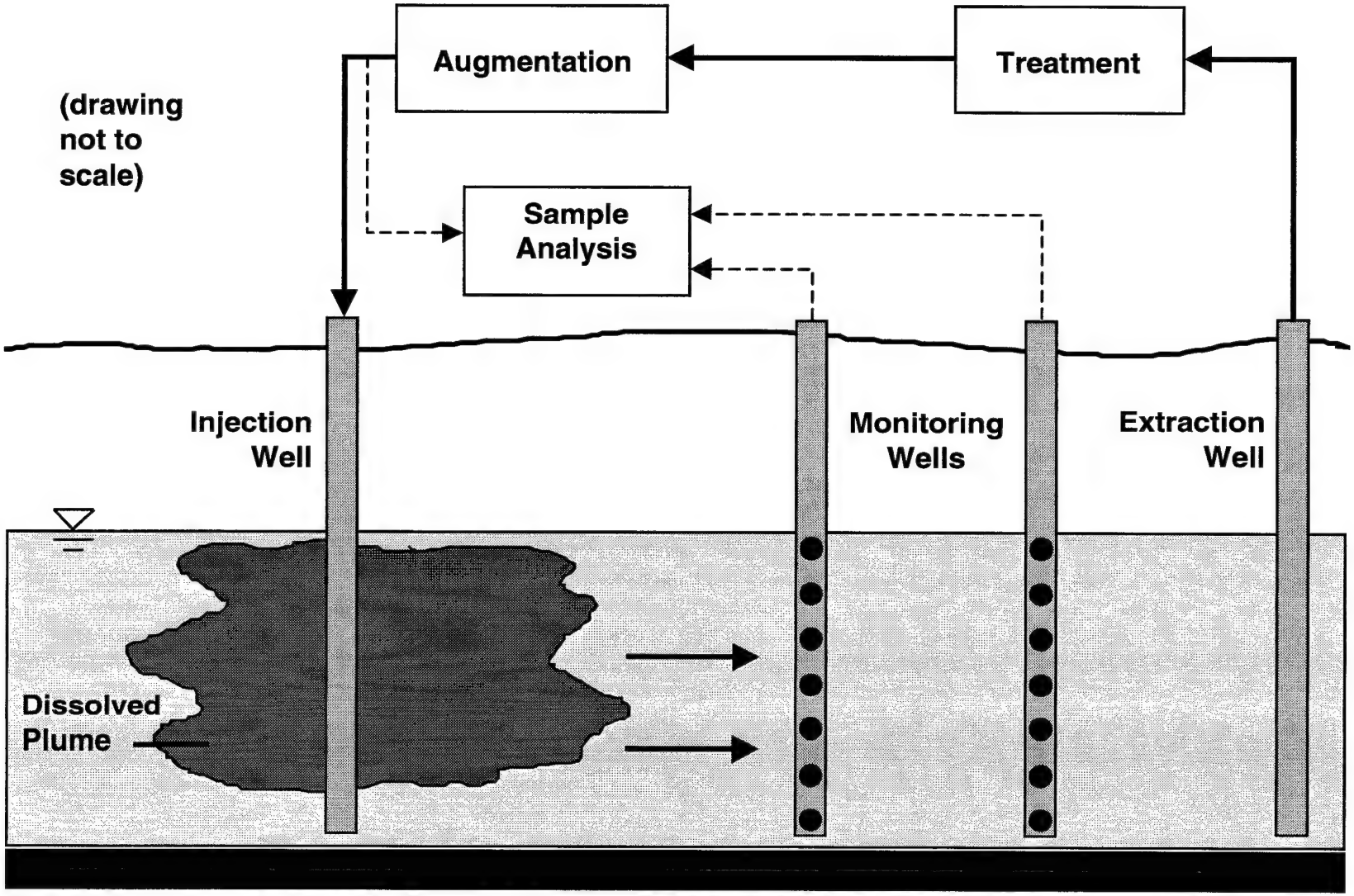

Figure 5. Schematic of injection/extraction well system.

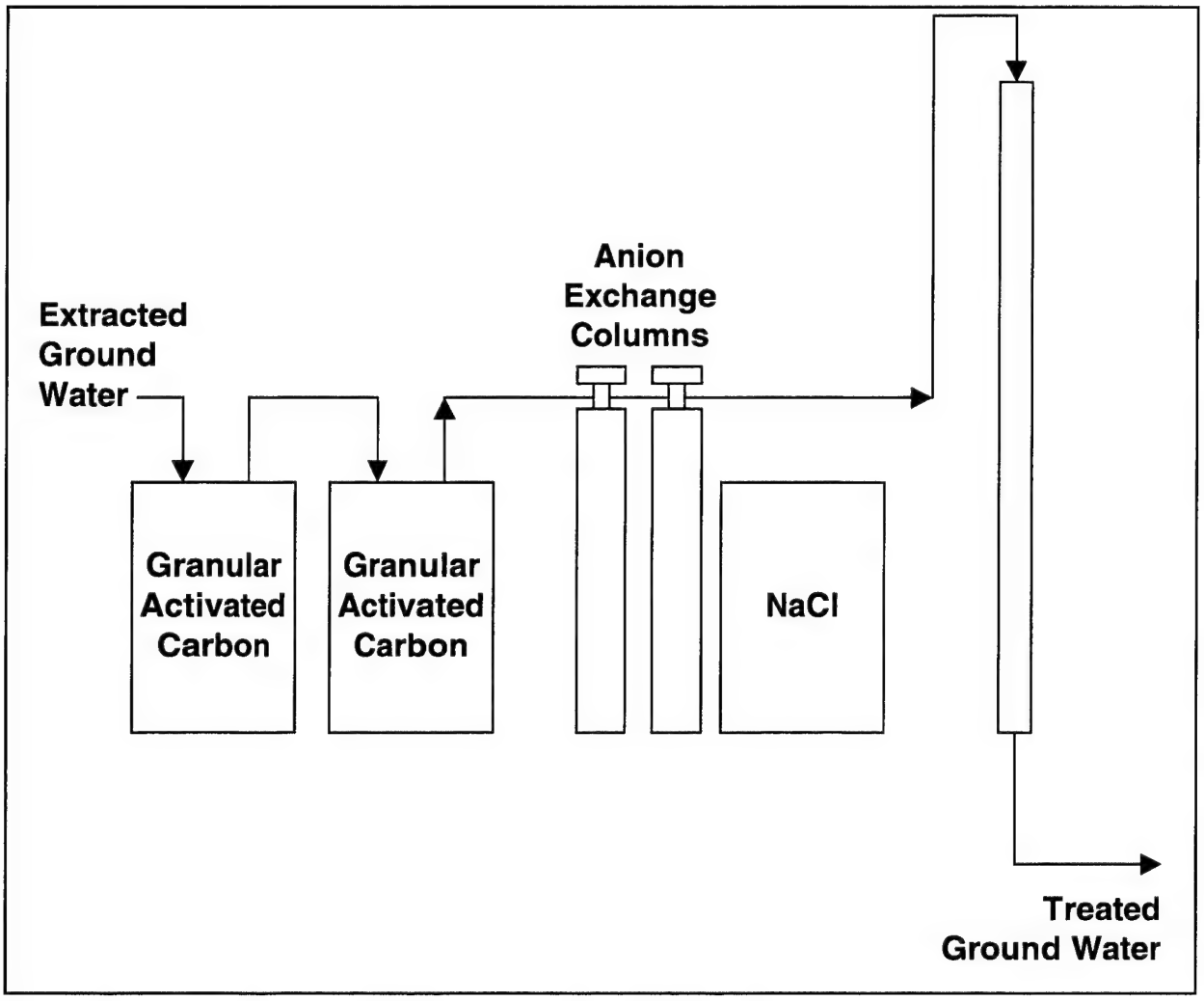

Figure 6. Schematic for the water treatment system that is used to remove hydrocarbons, anions, and gases from extracted water.

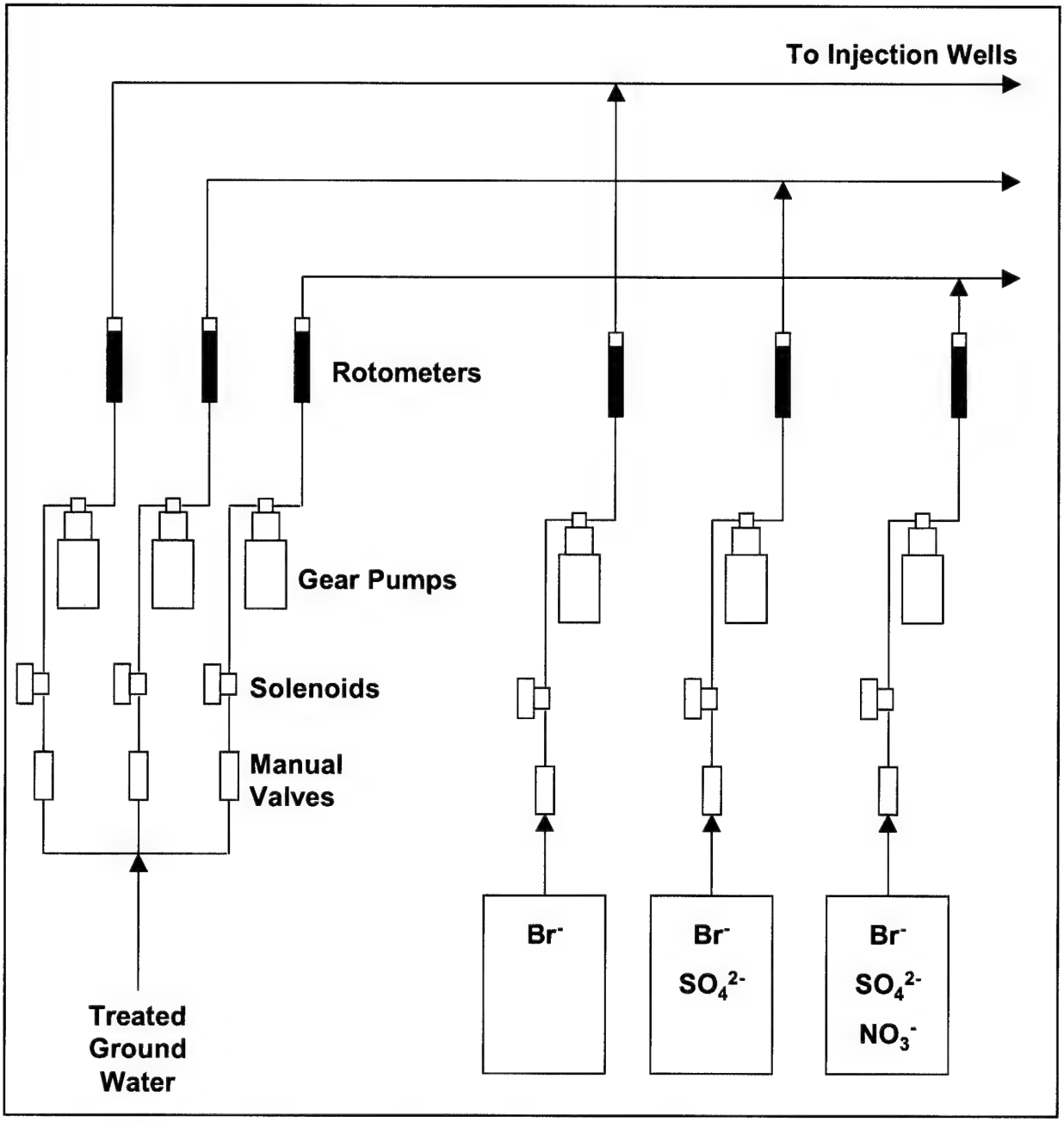

Figure 7. Schematic for the chemical delivery system that is used to augment water with sulfate and/or nitrate prior to re-injection.

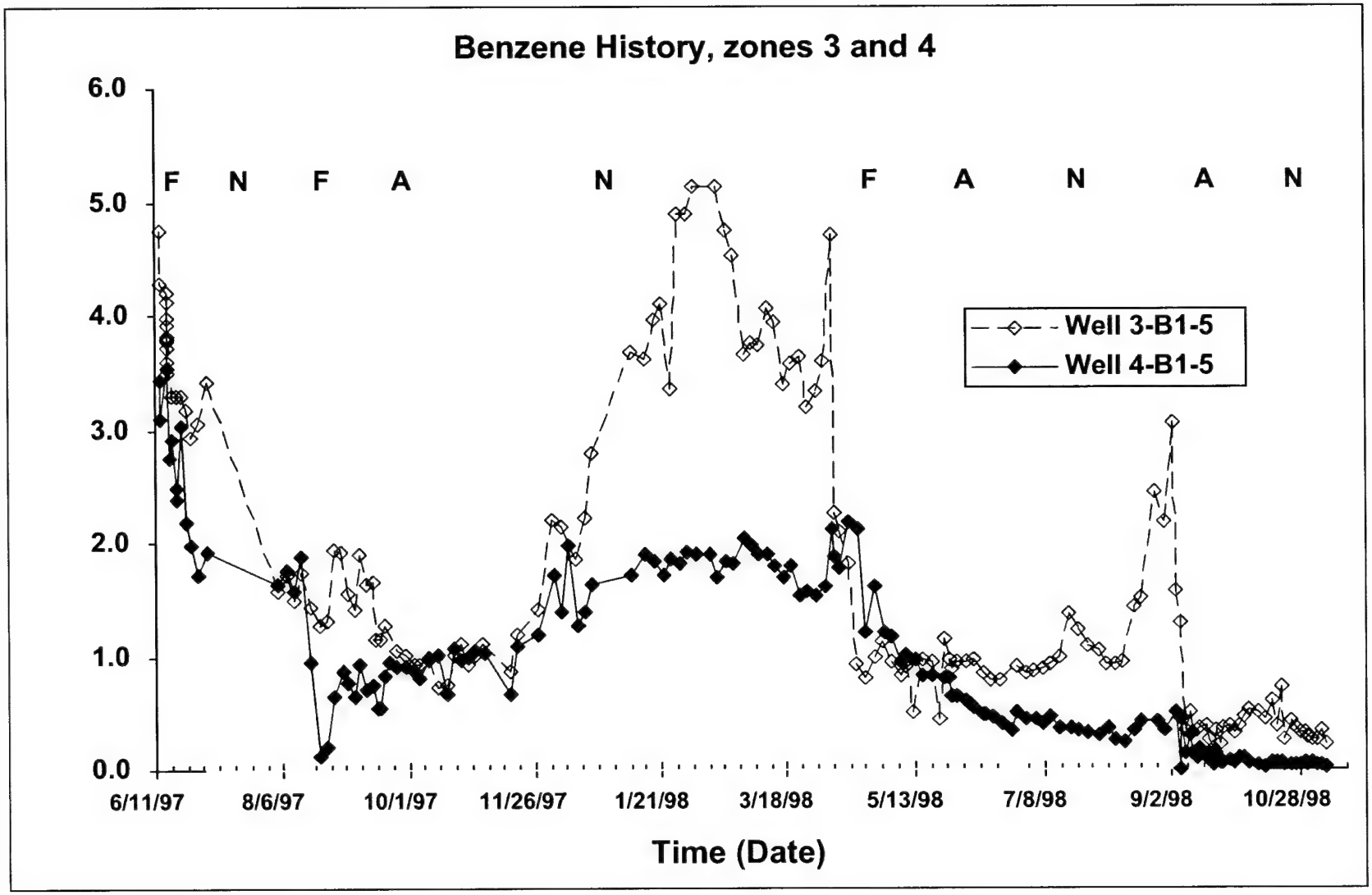

Figure 8. Benzene concentration histories at monitoring Points 3-B1-5 and 4-B1-5.

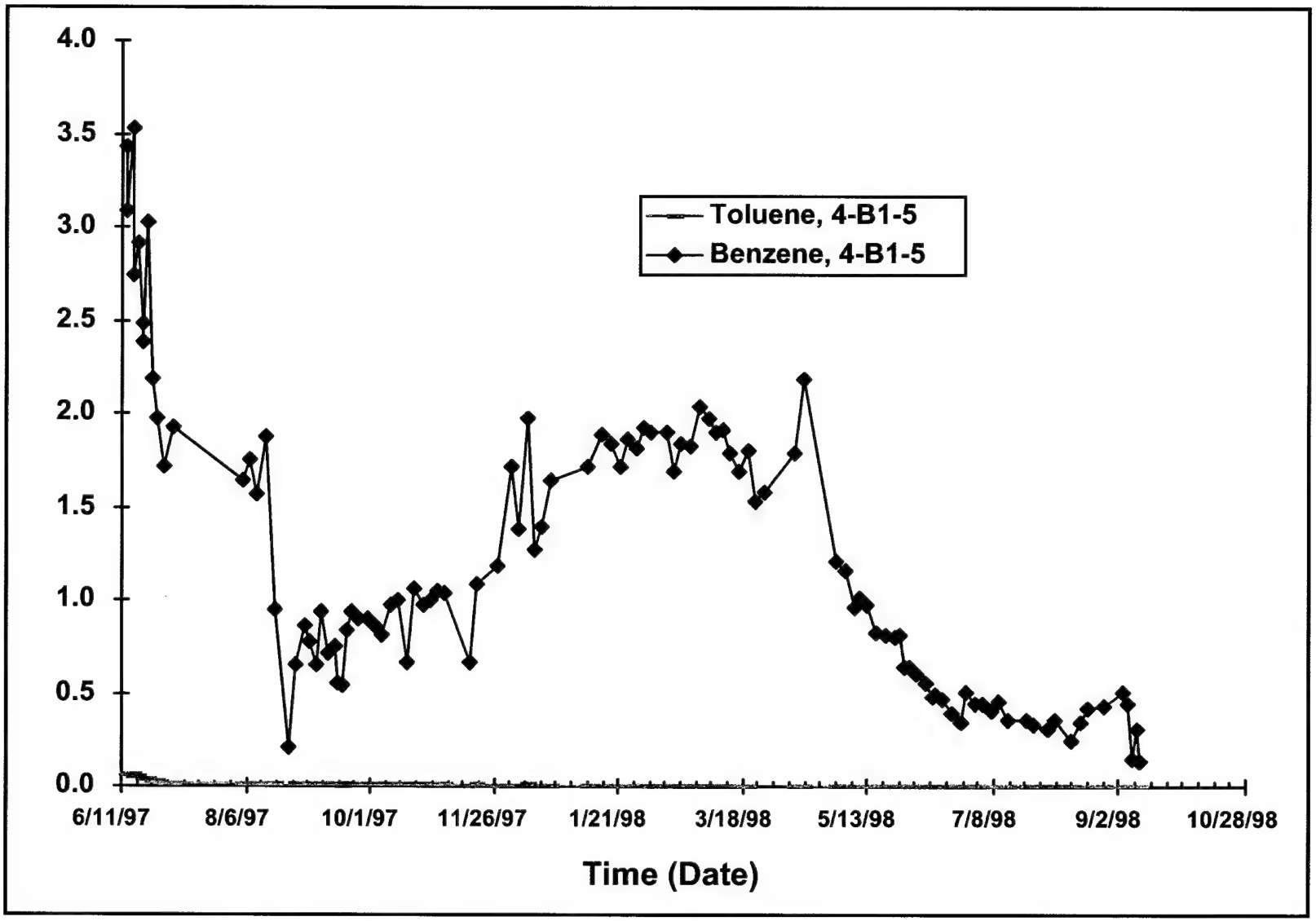

Figure 9.Toluene and benzene concentration histories at Point 4-B1-5.
Toluene concentrations are near zero even at the start of the demonstration.

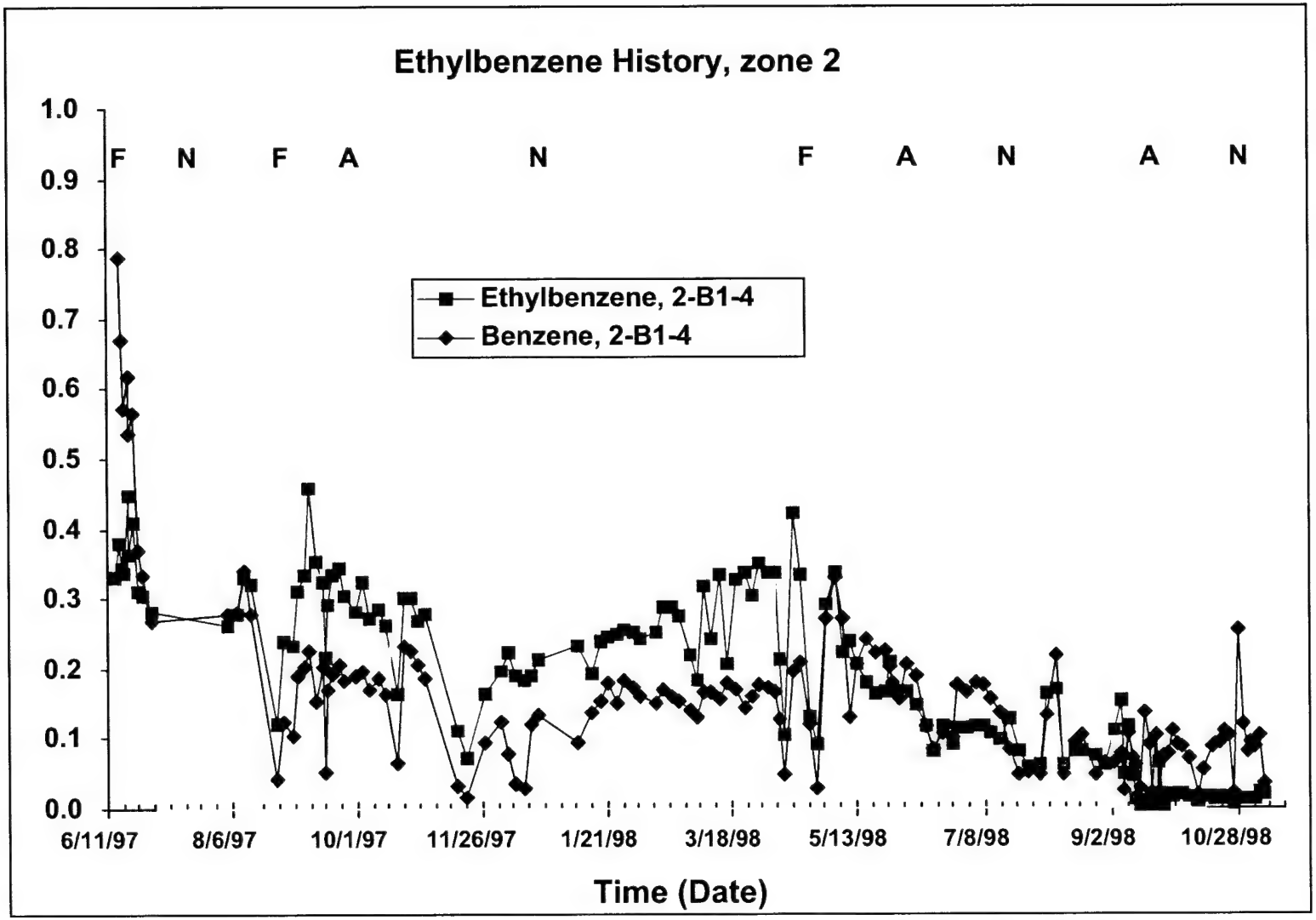

Figure 10. Ethylbenzene and benzene concentration histories at monitoring Point 2-B1-4.

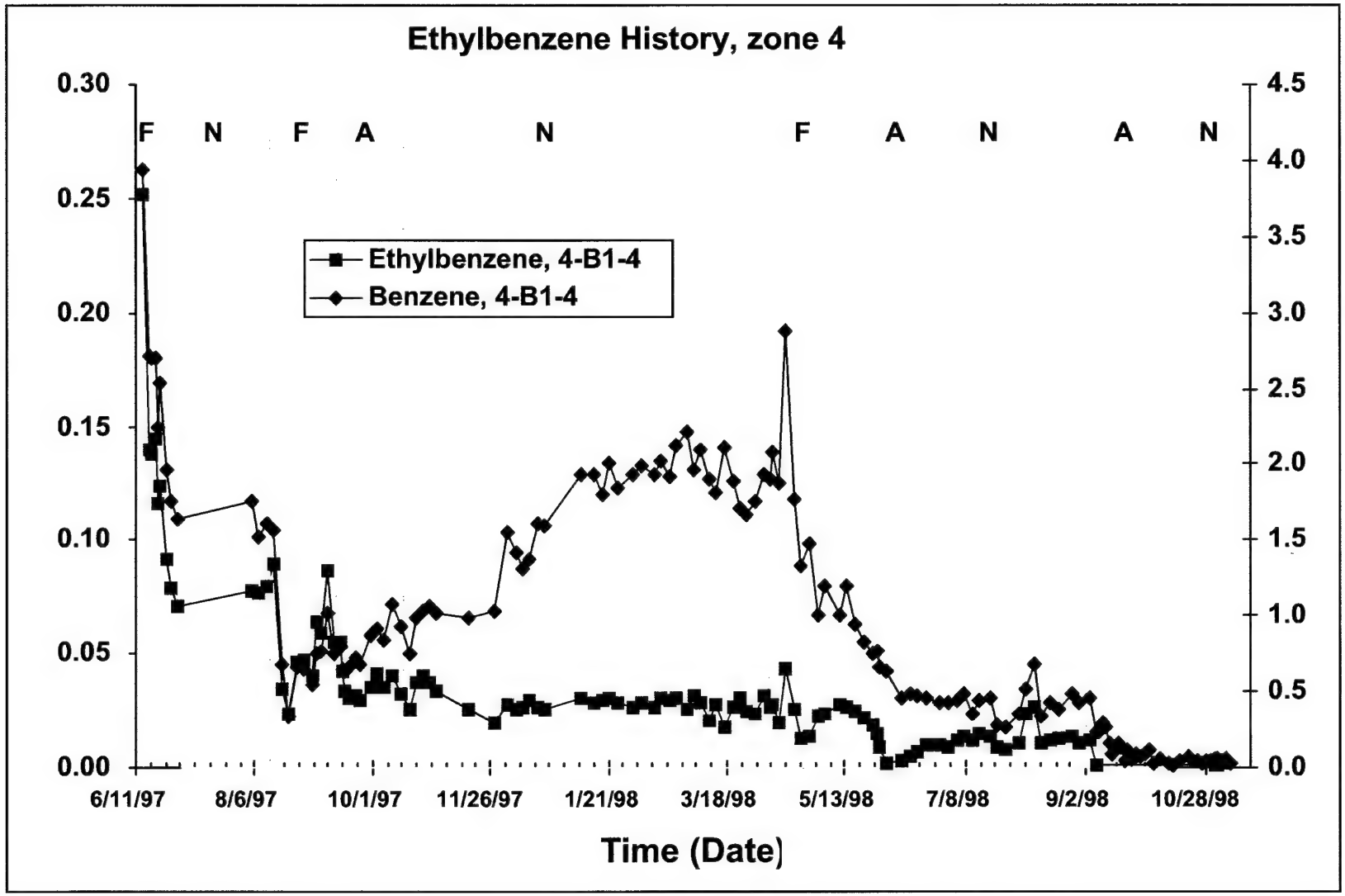

Figure 11. Ethylbenzene and benzene concentration histories at monitoring. Point 4-B1-4.

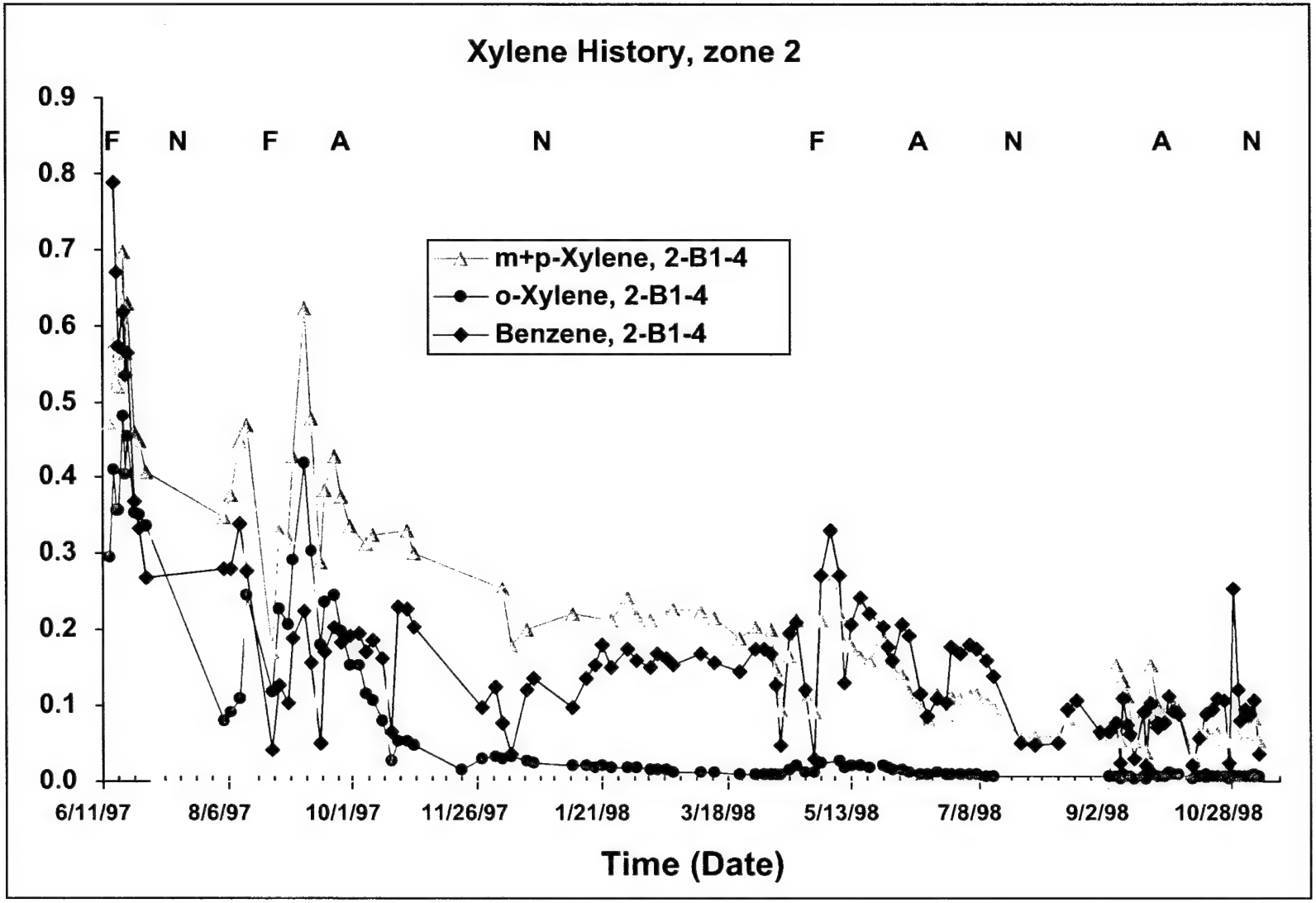

Figure 12. Concentration histories of xylene isomers and benzene at monitoring. Point 2-B1-4.

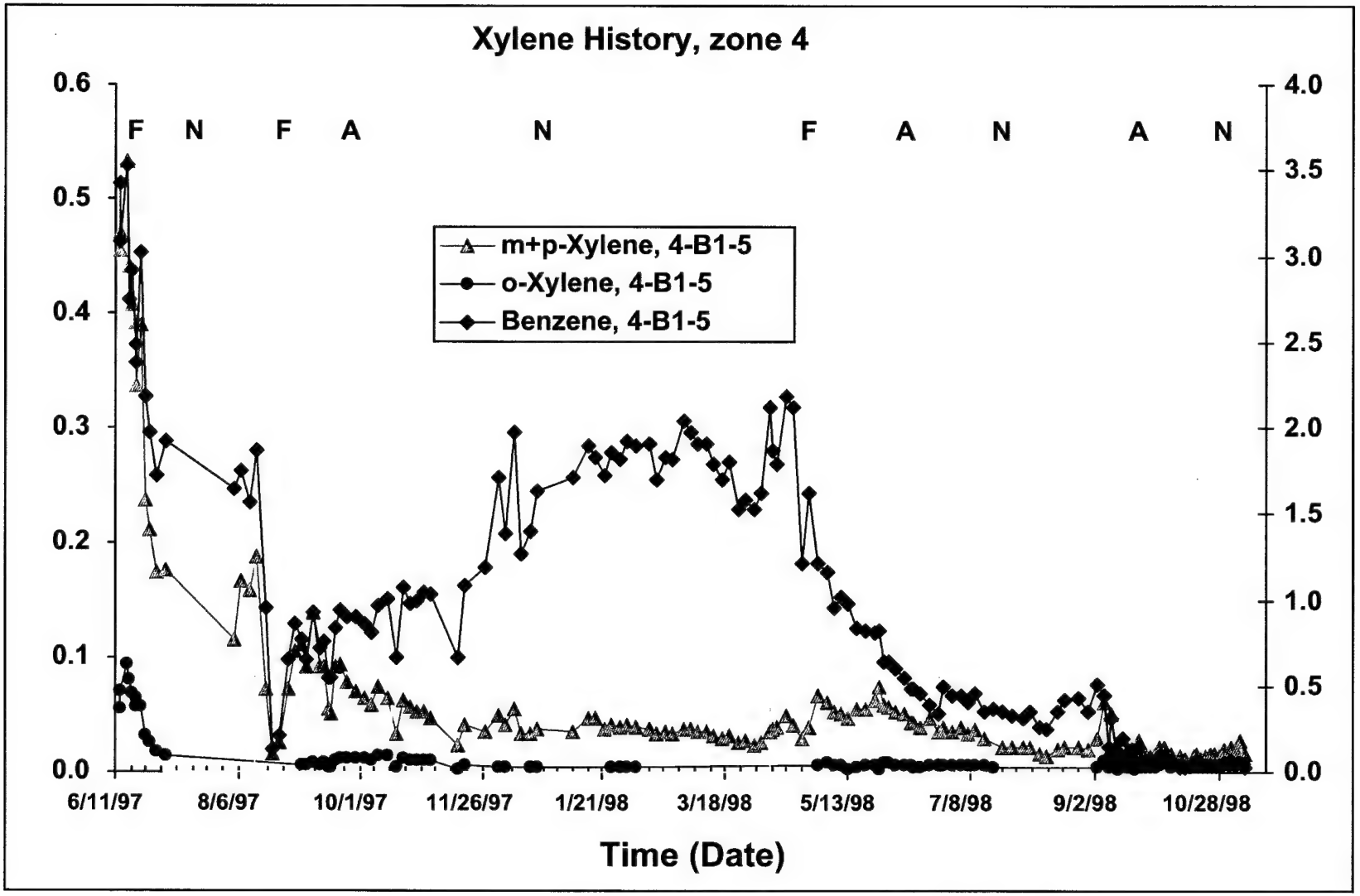

Figure 13. Concentration histories of xylene isomers and benzene at monitoring. Point 4-B1-5.

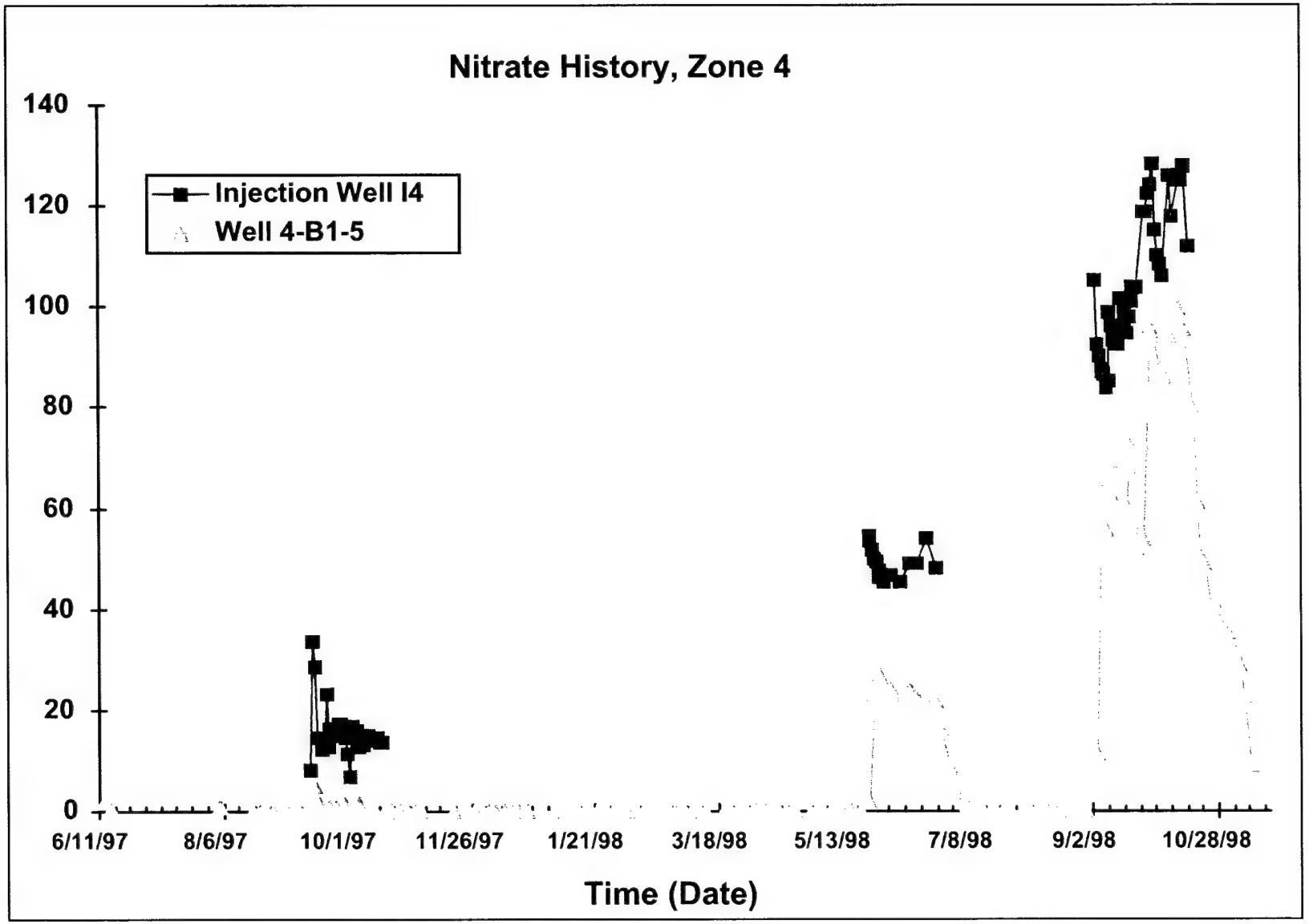

Figure 14. Nitrate concentration histories at injection well I4 and at monitoring Point 4-B1-5.

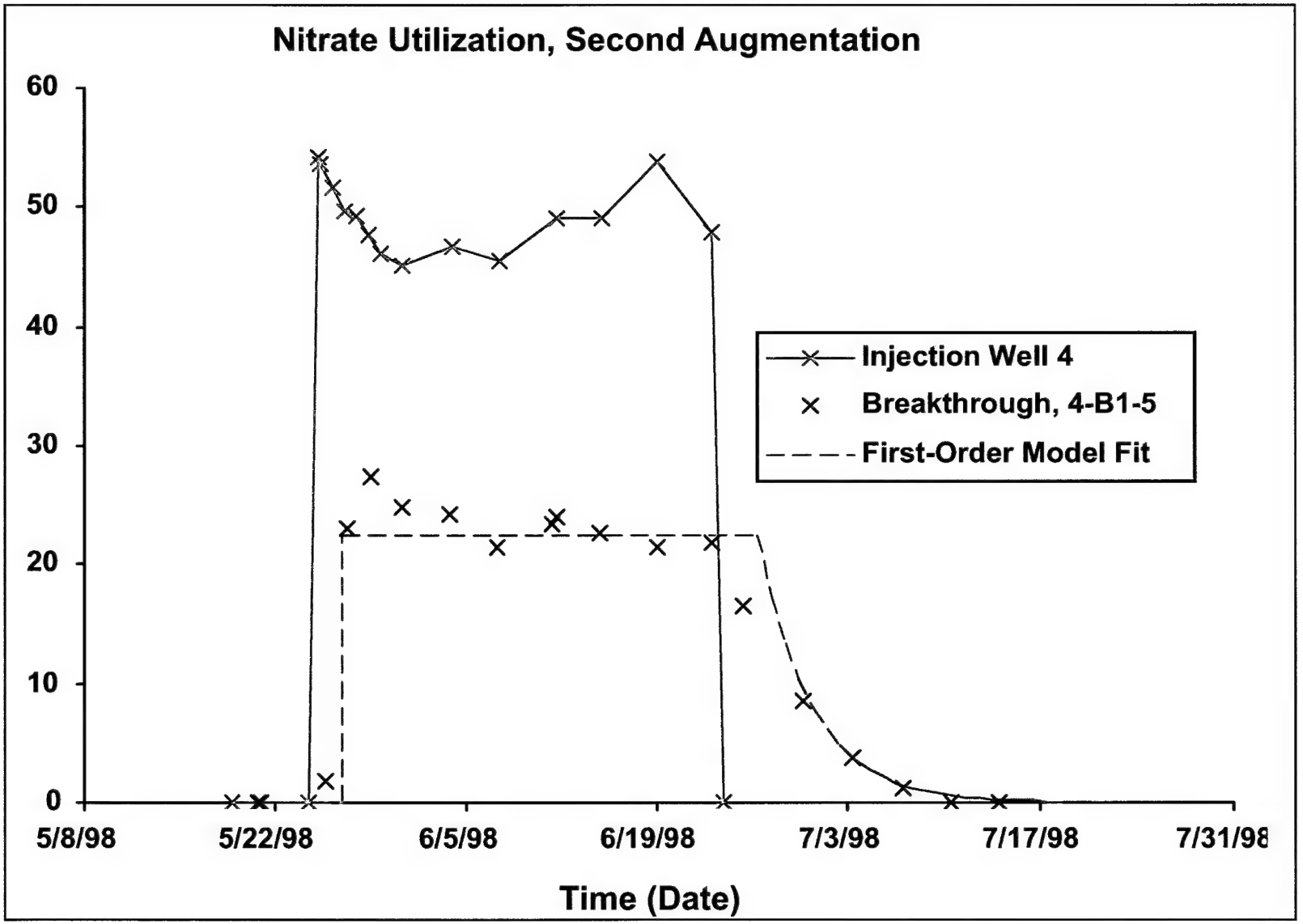

Figure 15. Nitrate utilization in zone 4 after second augmentation.

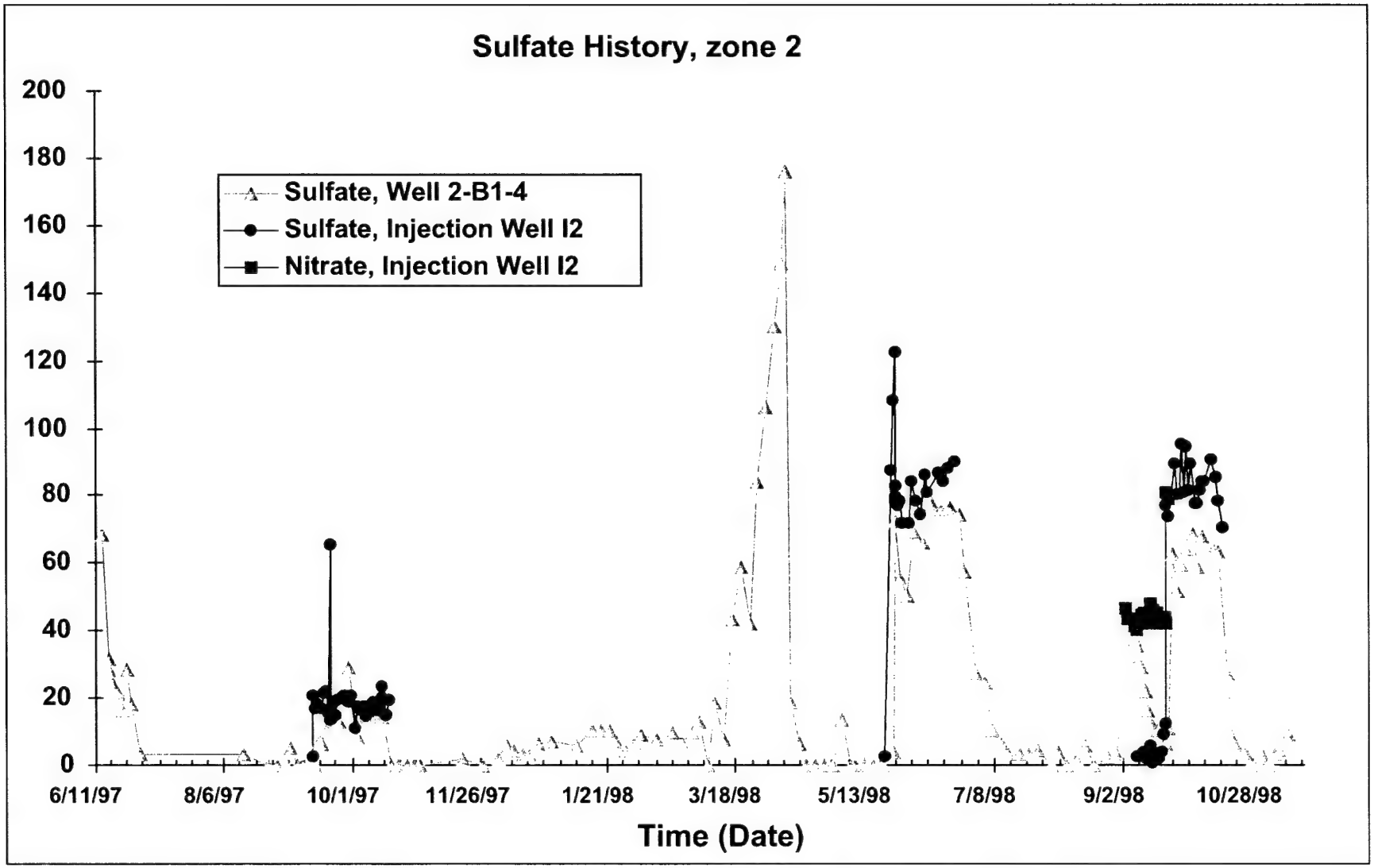

Figure 16. Sulfate and nitrate concentration histories at injection well I2, and sulfate concentration history at monitoring Point 2-B1-4.

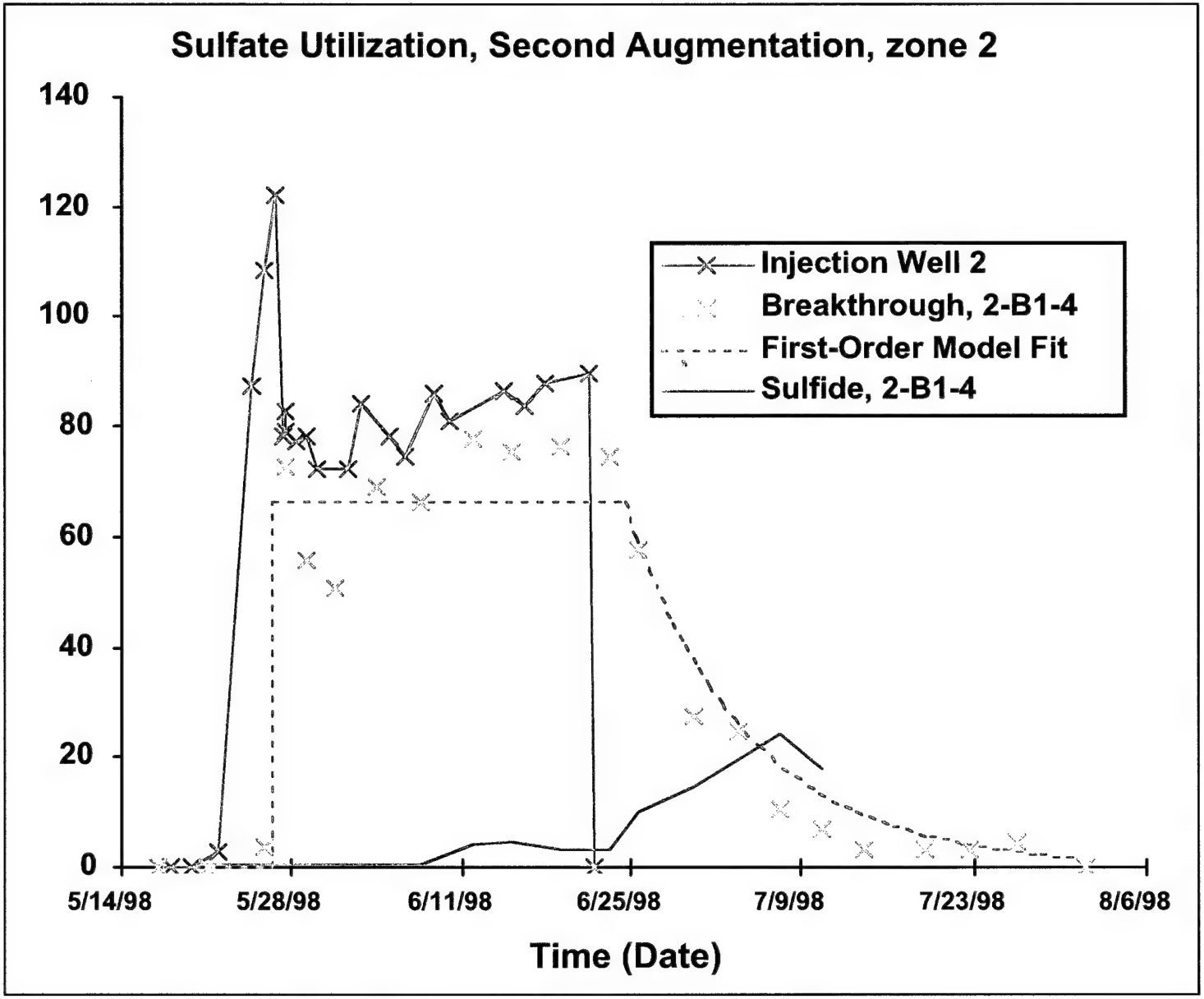

Figure 17. Sulfate utilization and sulfide generation in zone 2 after second augmentation.

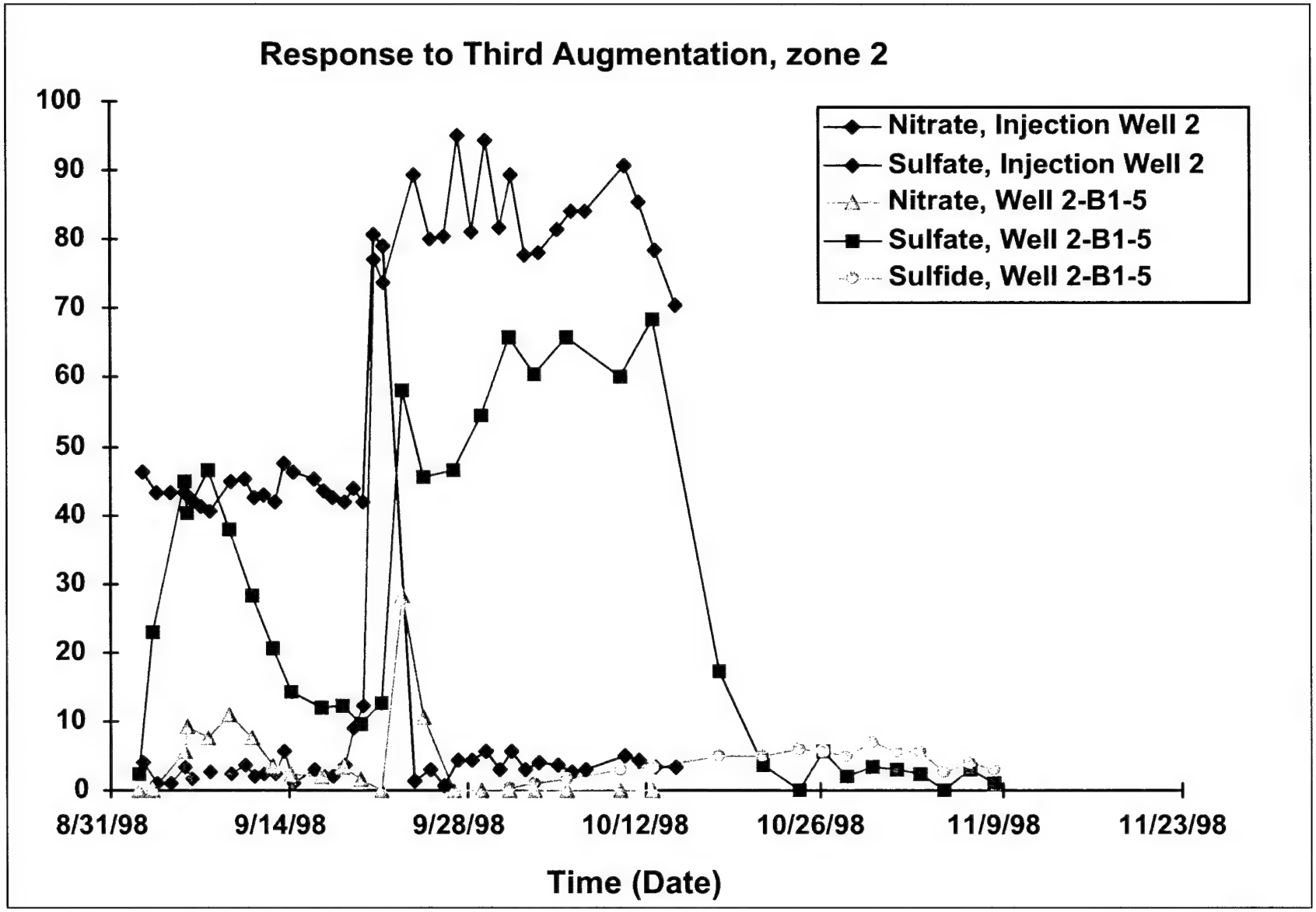

Figure 18. Nitrate and sulfate utilization and sulfide generation in zone 2 after third augmentation.

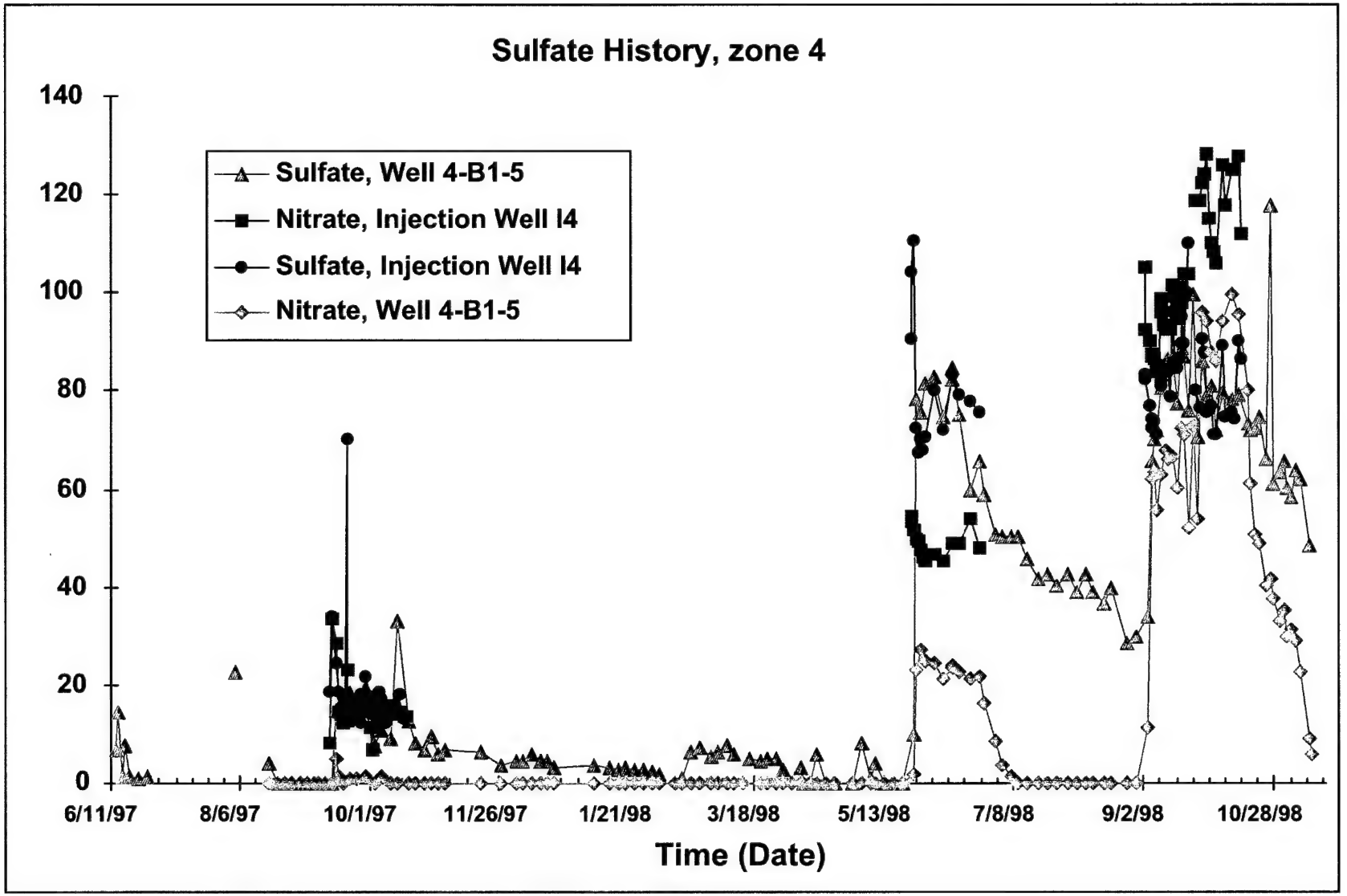

Figure 19. Sulfate and nitrate concentration histories at injection Well I4 and at monitoring Point 4-B1-5.

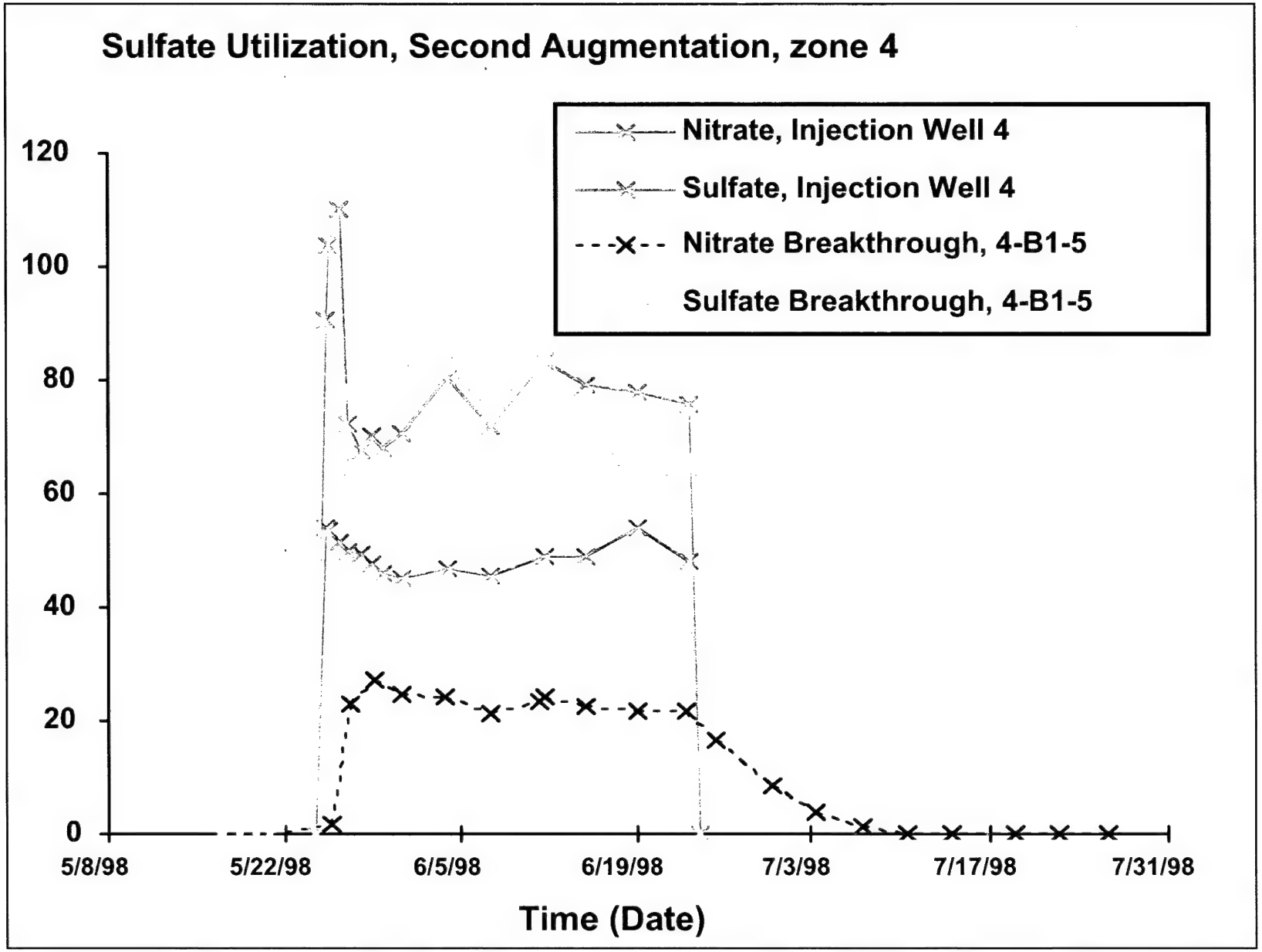

Figure 20. Simultaneous sulfate and nitrate utilization in zone 4 after second augmentation.

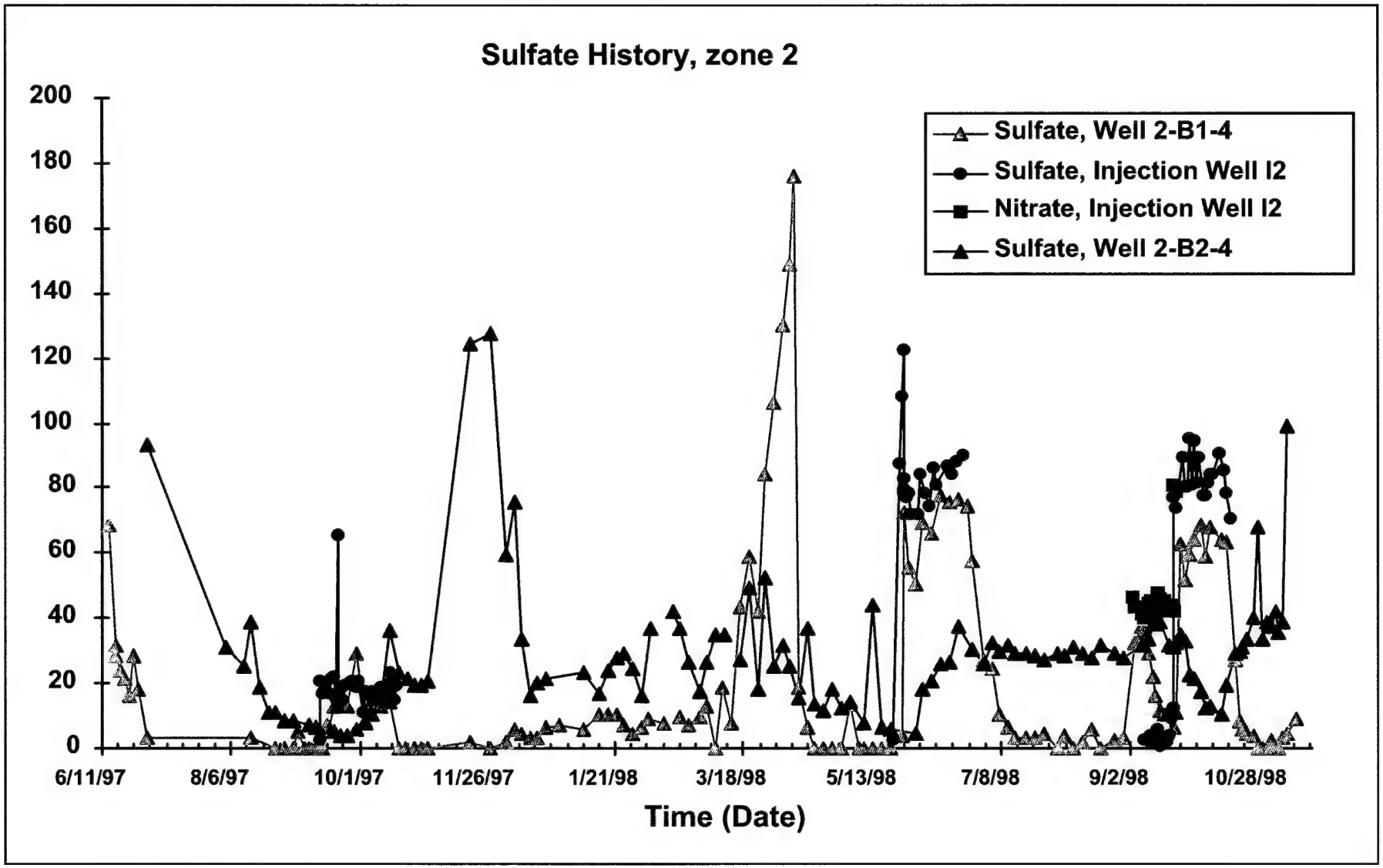

Figure 21. Sulfate and nitrate concentration histories at injection Well I2 and sulfate concentration history at Wells 2-B1-4 and 2-B2-4.

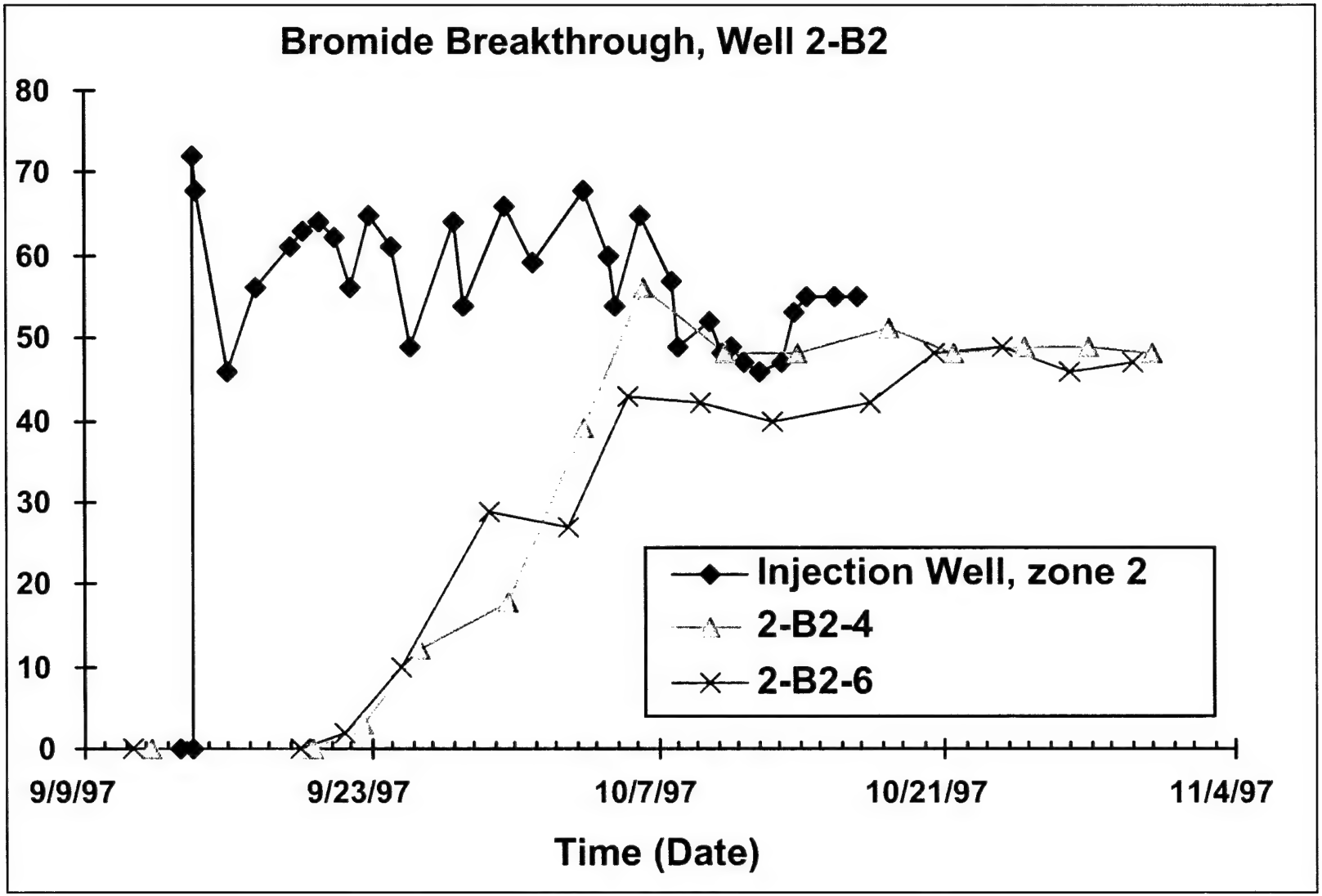

Figure 22: Bromide breakthrough curves at monitoring Wells 2-B2-4 and 2-B2-6.

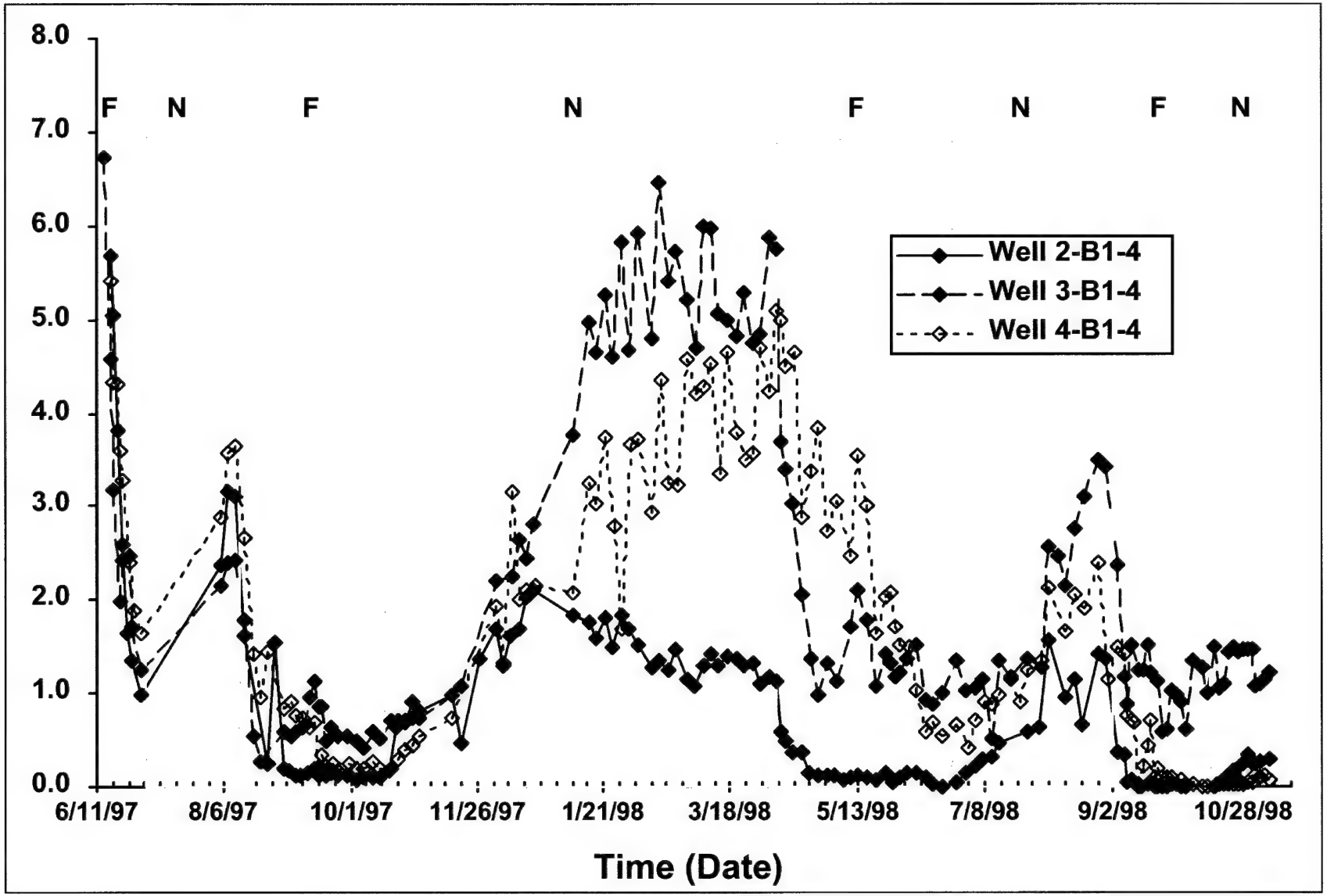

Figure 23. Methanogenesis in the three different treatment zones.

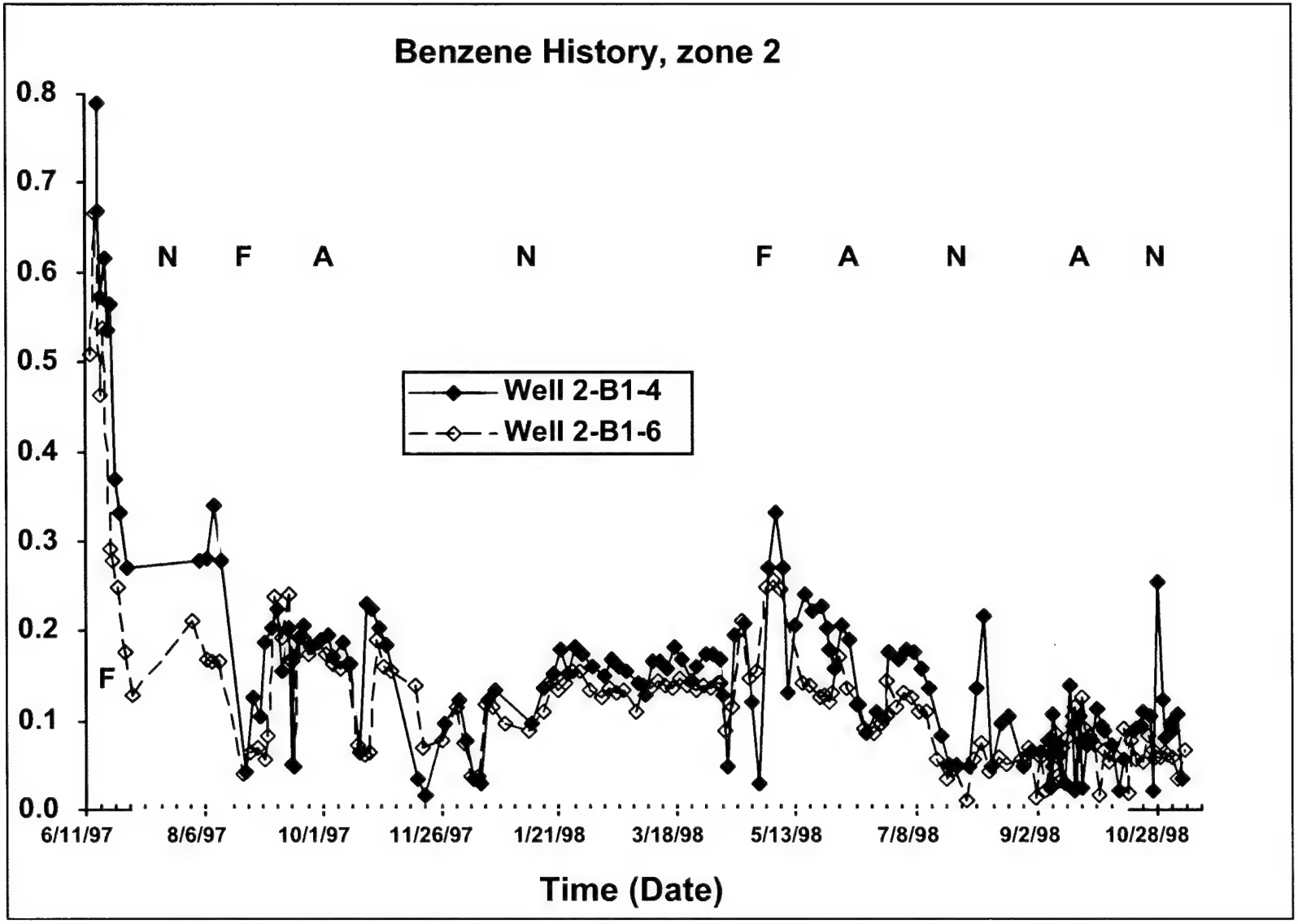

Figure 24. Comparison of measured benzene concentrations at two different veritcal locations - Wells 2-B1-4 and 2-B1-6.

Appendix A
Contact Information for Demonstration Participants

Project Management:
Carmen A. LeBron
Naval Facilities Engineering Service Center (NFESC)
Restoration Development Branch
1500 23rd Ave., ESC-411
Port Hueneme, CA 93043
Tel.: 805-982-1616
Fax: 805-982-4304
E-mail: lebronca@nfesc.navy.mil

Principal Investigator:
Martin Reinhard
Department of Civil and Environmental Engineering
Stanford University
Stanford, CA 94305-4020
Tel.: 650-723-0308
Fax: 650-725-3162
E-mail: reinhard@cive.stanford.edu

Site Management:
Gary Hopkins
Department of Civil and Environmental Engineering
Stanford University
Stanford, CA 94305-4020
Tel.: 408-262-2070
E-mail: hopkins@cive.stanford.edu

Site Oversight:
Paul D. Nguyen
Naval Weapons Station
Code #092 Bldg. 230
Seal Beach, CA 90470-5000
Tel.: 310-626-7011

Regulatory Oversight:

Lawrence Vitale
California Reg. Water Quality Control Board, Region 8
2010 Iowa Ave., Suite 100
Riverside, CA 92507-2409
Tel.: 909-782-4130

Appendix B
Technology Demonstration Plan

Modified September 1996

ESTCP

Technology Demonstration Plan

for

Enhanced In Situ Anaerobic Bioremediation of Fuel-Contaminated Ground Water

Martin Reinhard, Peter K. Kitanidis,
Gary D. Hopkins
Department of Civil Engineering
Stanford University
Stanford, CA 94305-4020

Tel 415-723-0308
Fax 415-725-3162

Carmen LeBron
Restoration Development Branch
Naval Facilities Engineering Service Center
Port Hueneme, CA 93043

Tel 805-982-1616
Fax 805-982-1592

PROJECT SUMMARY

The purpose of this project is to demonstrate enhanced intrinsic bioremediation of aquifers contaminated with fuel hydrocarbons. Indigenous microorganisms have been shown to oxidatively destroy hydrocarbon contaminants to carbon dioxide, both, aerobically (in the presence of oxygen) and anaerobically (in the absence of oxygen). Under anaerobic conditions, nitrate, ferric iron, sulfate or carbon dioxide may serve as the electron acceptor (oxidant). For the process to proceed at acceptable rates, enhancement, i.e., engineered intervention, may be necessary. Enhancement may entail either augmenting the contaminated zone with electron acceptor(s), removing inhibiting products, or both. Under favorable conditions, depending on the geochemical and hydrogeological conditions, the prevailing ground water flow may supply sufficient doses of electron acceptors and remove excess products at rates that render engineered stimulation unnecessary. At the Seal Beach site, the regional ground water velocity is very small. Previous studies at the site indicate that the supply of electron acceptors and/or the removal of inhibitors are limiting. The site is therefore well suited for evaluating the enhancement of intrinsic bioremediation.

Intrinsic bioremediation promises to be a competitive treatment technology because the contaminants are destroyed utilizing the contaminated subsurface as a natural treatment zone with no or minimal engineered intervention. The focus of the technology demonstration will be on the aromatic hydrocarbon contaminants benzene, toluene, ethylbenzene and the o-, m- and p-xylene isomers (BTEX) and on the electron acceptors nitrate, sulfate, and carbon dioxide. The technology will be demonstrated at a historic gasoline-contaminated site located on the premises of the Seal Beach Naval Weapons Station.

Three different treatment zones denoted T1, T2 and T3 will be established in a subsection of the contaminated aquifer. Zone T1 will be fed with water that does not contain electron acceptors (other than carbon dioxide) to create a methanogenic treatment zone. Zone T2 will be fed water containing a limiting amount of sulfate to create a sequence of sulfidogenic followed by methanogenic conditions. Zone T3 will be fed water containing limiting amounts of nitrate and sulfate to create a sequence of nitrate-reducing, sulfate-reducing, and methanogenic conditions.

This objectives of this technology demonstration are to:

(1) Validate the technical viability of enhanced intrinsic anaerobic bioremediation;

(2) Develop cost data; and,

(3) Technology transfer.

The demonstration will last three years starting January 1995 and will proceed in three phases. Phase one will last approximately nine months and will involve development of the hydraulic flow field, analytical facilities, calibration of the hydraulic model and the development of three treatment zones, each approximately 90 m^3 in size. Phase two will last approximately 24 months and will include the optimization and field demonstration of the anaerobic treatment processes. During the remaining three months of the project, the results from the data will be evaluated and a final report will be written.

I. INTRODUCTION

I.A. Demonstration Purpose and Background

The overall goal of this project is to demonstrate and evaluate the efficacy of enhanced intrinsic anaerobic bioremediation of fuel-contaminated ground water. Anaerobic bioremediation technology utilizes the biodegradation potential of anaerobic bacteria for mineralizing fuel derived hydrocarbons. The technology consists of feeding water containing alternate electron acceptors to a contaminated aquifer to maximize biological hydrocarbon mineralization. To maximize the efficiency of bioremediation, the feed water stream will be treated to remove products that slow down the process of biotransformation.

Specific objectives of the demonstration include:

(1) Demonstration of the technical viability of enhanced intrinsic anaerobic bioremediation of fuel contaminated ground water,

(2) Development of cost data, and

(3) Preparation of a technology transfer package.

The demonstration targets benzene, toluene, ethylbenzene and o-, m- and p-xylene (BTEX). Other aromatic and aliphatic hydrocarbon compounds typically present in petroleum-derived fuels will also be studied, but with lower priority. The project involves application of previous laboratory and pilot-scale research to a large field site. The evaluation involves three test zones approximately 90 m^3 in size; this size is sufficiently small to complete four evaluations within the three year project period, but large enough to allow for extrapolation to full-scale site cleanups. The information developed in this project will allow remediation contractors, consultants, regulators, responsible parties and the public to better evaluate anaerobic in situ bioremediation as an option for remediating sites contaminated with hydrocarbon fuels.

The discovery of the anaerobic biotransformation of BTEX compounds is relatively new and our understanding of the process and the controlling factors is still incomplete. However, recent laboratory and field work has shown that anaerobic BTEX degradation can be rapid if conditions are favorable. The goal of this project is to demonstrate that anaerobic microbial processes can potentially be used for site cleanup and should be considered in the treatment options for gasoline and other fuel-contaminated sites. Furthermore, the results of this demonstration should contribute to the regulatory acceptance of this technology.

Most of the insight into anaerobic biotransformation of BTEX compounds has been obtained from laboratory studies. BTEX transformation has been demonstrated in microcosms under denitrifying conditions (e.g. Zeyer et al. 1986, Hutchins et al. 1993, Barbaro et al. 1992), sulfate-reducing conditions (e.g. Beller et al. 1992, Edwards and Grbic-Galic 1992; Edwards et al., 1992), iron (III)-reducing conditions (Lovley and Lonergan 1990) and methanogenic/fermentative conditions (Wilson et al., 1986, Grbic-Galic and Vogel, 1987). When present as a mixture, the removal of BTEX compounds tends to be selective, and in some cases cometabolic. Most studies found toluene to be the most readily degraded BTEX compound and benzene was often found to be the least degraded compound. In a study reported by Edwards and Grbic-Galic (1992) with Seal Beach sediment as the inoculum, benzene was slowly oxidized to carbon dioxide under presumed sulfidogenic conditions. More recently, in microcosms studies reported by Lovely et al. (1994 and

1995) the degradation of benzene was shown to be rapid under iron(III) and sulfate reducing conditions. Contaminated marine sediments and sediments from a shallow fresh water aquifer were used to construct the sulfate-reducing and iron(III)-reducing microcosms.

Although laboratory studies have conclusively demonstrated anaerobic BTEX degradation, there is a paucity of field data that demonstrate the process at the field scale. As a consequence, it has been difficult to take advantage of intrinsic anaerobic bioremediation. This is unfortunate since the potential benefits could be very significant. So far, few attempts have been made to demonstrate anaerobic bioremediation at the field scale under controlled conditions and the few reported field demonstrations have been made under denitrifying conditions only (Barbaro et al. 1992; Hutchins et al. 1991).

I.B. Technology Selection

Bioremediation is one of a limited number of options for restoring fuel-contaminated aquifers. In situ bioremediation utilizes naturally-occurring microorganisms capable of degrading organic contaminants. Technically, two goals must be accomplished:

(1) Supply of nutrients and/or electron acceptors to the contaminated zone for stimulation of microbial growth; and,

(2) Removal of metabolic products that inhibit or interfere with the bioremediation process.

Using contaminants as substrates for energy and growth and an electron acceptor such as oxygen, nitrate or sulfate, microorganisms convert the contaminants into harmless products, principally CO_2 and water, in addition to cell mass, inorganic salts. Denitrification may produce nitrogen gas and sulfate reduction may produce hydrogen sulfide. Oxygen is the preferred electron acceptor and is used first. After oxygen is consumed, anaerobic microorganisms will use a series of alternate electron acceptors. As indicated below, under anaerobic conditions with nitrate or sulfate as the electron acceptor, the final products are nitrogen gas and hydrogen sulfide, respectively; and under methanogenic/fermentative conditions, the final products are methane and carbon dioxide. In designing anaerobic bioremediation processes, the formation of these products must be considered. The principal advantage of intrinsic bioremediation over conventional pump-and-treat technologies is that the contaminants are destroyed in situ and no secondary waste streams are produced needing further treatment.

The conventional approach to hydrocarbon bioremediation is based on aerobic processes. Anaerobic bioremediation has been tested only in a very few cases and is still considered experimental. For instance, in a review of 17 sites contaminated with hydrocarbon fuels and oils (Staps, 1990), hydrogen peroxide (source of oxygen) was used as the electron acceptor at seven sites, air at five, combinations of nitrate-ozone and nitrate-air at one site each, and nitrate alone was used at three sites. The demonstration will utilize methanogenic conditions in zone T1, and sequential redox conditions of sulfate-reduction and methanogenic conditions in T2, and nitrate-reducing, sulfate-reducing and methanogenic conditions in T3. These redox conditions have been evaluated previously in small scale field tests discussed below.

The principal factors that must be considered when designing anaerobic bioremediation schemes include all aspects affecting (1) microbial degradation, (2) contaminant retardation, (3) advection and dispersion, (4) site specific source- or sink-processes such as volatilization into the unsaturated zone and dissolution of non aqueous phase liquids (NAPLs).

(i) Microbial Degradation

The factors affecting the rate of biotransformation, include the abundance and nutritional status of the microflora, the type and quantity of electron acceptors present, catabolic inhibition, toxicity, and geochemical factors such as solubility limitation, precipitation, and abiotic redox processes. At present, these factors are difficult to quantify, especially under anaerobic conditions. Electron acceptors other than oxygen are termed "alternate". The most commonly occurring alternate electron acceptors include nitrate, sulfate, iron(III), and carbon dioxide. Electron acceptors tend to be used successively in order of decreasing free energy yield. Hence, oxygen tends to be the preferred electron acceptor, followed by nitrate, manganese(IV) and iron(III) oxides (MnO_2 and FeOOH, respectively), sulfate, and carbon dioxide. This sequence applies to pH 7 and should be valid for most field conditions where the appropriate microorganisms occur. The stoichiometries of the five biooxidation processes, aerobic, nitrate-reducing, ferric iron-reducing, sulfate-reducing and methanogenic/fermentative, are briefly reviewed using toluene as a representative BTEX compound.

Rapid aerobic degradation requires ample supply of nutrients and oxygen, good mixing, and a high microbial mass, conditions that are difficult to maintain in aquifers (Wilson et al. 1986; Lee et al. 1988). Furthermore, at many sites there may be a very high abiotic oxygen demand due to hydrogen sulfide, Fe^{2+} or other readily oxidizable compounds, making it difficult to increase the reduction potential into the aerobic range (greater than 0.82 V) .

A range of other, site-specific factors can limit biotransformation, such as the occurrence of metals or other toxics, accumulation of toxic intermediates and sub-optimal temperatures. Near NAPL, contaminant concentrations may reach toxic levels thereby limiting biological activity. It is unknown whether aerobic or anaerobic processes are more readily inhibited by such factors. Thus, the decision to use either aerobic or anaerobic processes may depend on site-specific conditions.

Aerobic Conditions
The aerobic biological degradation of toluene ignoring cell growth can be expressed as:

$$C_7H_8 + 9\ O_2 \rightarrow 7\ CO_2 + 4\ H_2O \qquad (1)$$

In this equation, the toluene is completely mineralized to carbon dioxide and water and the formation of biomass is not considered. From the above equation, biodegradation of 1 mg/L of toluene dissolved in ground water requires 3.1 mg/L of oxygen. Since pure oxygen has a solubility of approximately 45 mg/L in water at 1 atmosphere pressure and 20°C, the maximum amount of hydrocarbon (as toluene) which can be degraded by water saturated with oxygen is only 14.5 mg/L. When air is used to saturate the water with oxygen, the dissolved oxygen concentration is only about 9 mg/L and the maximum amount of hydrocarbon (as toluene) which can be degraded by water saturated with air would be only 2.9 mg/L. Thus, for the bioremediation of 1 kg of aquifer material containing 10 g/kg hydrocarbons, a minimum of 3.1 m^3 of oxygenated water containing 10 mg/L O_2 must be supplied. Thus, the mass transfer of the oxygen becomes the limiting process for enhanced aerobic in situ bioremediation of hydrocarbon contaminated sites.

Hydrogen peroxide, an alternative source of oxygen, may be supplied to an aquifer for enhanced aerobic bioremediation (US Patent No. 3,846,290, Nov. 5 1974). However, the addition of excess hydrogen peroxide can easily lead to oxygen bubble formation, potentially causing the aquifer to plug especially if the aquifer formation is sandy in nature. Although using hydrogen

peroxide increases the available oxygen to the aquifer, the increased costs of using hydrogen peroxide and the potential complications arising from the use of hydrogen peroxide must also be considered.

Denitrifying Conditions

The stoichiometry for the complete biodegradation of toluene to carbon dioxide under nitrate reducing conditions assuming no cell growth is as follows:

$$C_7H_8 + 7.2\ H^+ + 7.2\ NO_3^- \text{ ---> } 3.6\ N_2 + 7.6\ H_2O + 7\ CO_2 \qquad (2)$$

From the above equation, 1 mg/L of toluene dissolved in ground water would require 4.8 mg/L of nitrate. Sodium nitrate can be used as the source of the nitrate. Sodium nitrate has a solubility of 670 g/L (as sodium nitrate). Although nitrate solubility is high, the process may become limited by the formation of nitrogen gas, which is relatively insoluble (20 mg/L at 20°C). Thus, the degradation of approximately 18 mg/L hydrocarbon (as toluene) using 88 mg/L of nitrate would result in nitrogen saturating the ground water. Note that if the ground water was initially air-saturated, degradation of approximately 3.6 mg/L of hydrocarbon fuel contamination would cause nitrogen saturation.

When biodegradation of mixtures of benzene, toluene, ethylbenzene and xylenes (BTEX) was tested under denitrifying conditions, degradation tended to be sequential, with toluene being the first substrate to be degraded, followed by the degradation of p- and m-xylene, ethylbenzene and o-xylene (Ball and Reinhard, 1995). Reports seem consistent in their findings that benzene is not degraded under nitrate-reducing conditions (Kuhn et al., 1988, Hutchins et al., 1991, Ball and Reinhard, 1995). Hutchins et al. (1991) reported longer lag times and slower degradation rates in core material contaminated with JP-4 aviation fuel than in uncontaminated core material.

Sulfate Reducing Conditions

Bioremediation using sulfate as the electron acceptor involves oxidation of aromatic hydrocarbons by sulfidogenic organisms coupled with reduction of sulfate to hydrogen sulfide (Haag et al. 1991, Beller et al. 1992, Edwards et al., 1992). Sulfate is commonly found in shallow ground water aquifers, especially those influenced by marine geochemical conditions. For toluene, the stoichiometry of this reaction, assuming no cell growth, may be written as (Beller et al., 1992):

$$C_7H_8 + 4.5\ SO_4^{2-} + 3\ H_2O \text{ ---> } 2.25\ HS^- + 2.25\ H_2S + 7\ HCO_3^- + 0.25\ H^+ \qquad (3)$$

According to this equation, 1 mg/L of toluene dissolved in ground water requires about 4.7 mg/L sulfate for microbial degradation. The reduced product, hydrogen sulfide is known to be toxic to some sulfate-reducing microorganisms at concentrations ranging from 1 to 3 mM (34-102 mg/L)(Beller and Reinhard, 1995).

In Seal Beach microcosms, degradation under sulfate-reducing conditions was sequential with toluene as the first substrate degraded, followed by p-xylene and o-xylene degraded last (Edwards et al., 1992). Ethylbenzene and benzene were not degraded under the conditions of the experiment. In a follow-up study, Edwards and Grbic-Galic (1992) observed benzene degradation in the absence of all other aromatic substrates. After a lag time of 30 days under strictly anaerobic conditions these authors observed mineralization of benzene and suspected sulfate to be the electron acceptor.

Iron(III) Reducing Conditions

Lovley and Lonergan (1990) have isolated an iron-reducing bacterium capable of degrading toluene, p-cresol and phenol. The stoichiometry for toluene degradation under iron reducing conditions is

$$C_7H_8 + 36\ Fe^{3+} + 21\ H_2O \text{ ---> } 36\ Fe^{2+} + 7\ HCO_3^- + 43\ H^+ \quad (4)$$

whereby 36 moles of Fe(III) are required to oxidize one mole of toluene. Relative to other anaerobic processes, Fe(III) reduction has a very unfavorable substrate to electron acceptor ratio. Lovley et al. (1989) found that toluene was transformed into CO_2 and Fe^{2+} at a ratio that agreed with the above stoichiometry.

Transport of the dissolved iron Fe(II) from the aquifer could cause secondary problems such as clogging and fouling of the aquifer. Furthermore, the supply of large amounts of colloidal iron(III)oxide or soluble Fe(III)citrate to an aquifer has not been tested. To develop bioremediation strategies based on iron reduction, a better understanding of occurrence, nutritional requirements, growth conditions and metabolism of iron-reducing bacteria must be developed.

Methanogenic Conditions

Under methanogenic/fermentative conditions, several aromatic hydrocarbons including benzene and toluene, have been shown to be transformed into CO_2 and methane (Grbic-Galic and Vogel, 1987). The culture originated from sewage sludge and was enriched under methanogenic conditions using ferulic acid as the only carbon source. Assuming no cell growth, the stoichiometry for the transformation reaction is

$$C_7H_8 + 5\ H_2O \text{ ---> } 2.5\ CO_2 + 4.5\ CH_4 \quad (5)$$

Accordingly, biodegradation of 1 mg/L toluene produces approximately 0.77 mg/L methane gas. The solubility of methane gas in water is about 20 mg/L. Thus about 26 mg/L of hydrocarbon contaminant, as toluene, would lead to the saturation of the ground water with methane gas, potential bubble formation, and changes in hydraulic characteristics of the aquifer.

The Combined Use of Electron Acceptors

Because of the biological and physico-chemical limitations associated with individual electron acceptors, the most efficient method to remediate a fuel-contaminated site is to use the maximum capacity of several electron acceptors by simultaneously supplying several electron acceptors. Although multiple electron acceptors will tend to be fed simultaneously, the use of the electron acceptors will be sequential according to decreasing energy yield. Consequently, a sequence of redox conditions will develop downgradient from the injection point. Each redox condition will contribute to hydrocarbon removal. Because nitrate is the preferred electron acceptor, the nitrate-reducing zone will develop first, followed by the sulfate-reducing zone and the fermentative/methanogenic zone.

When using multiple electron acceptors, the limitations of each individual electron acceptor must be considered with respect to solubility limitations and potential chemical and biological interactions.

Removal of Reduced Products from the Feed Stream

Under denitrifying conditions, production of nitrogen gas above the removal capacity of the aquifer may cause clogging problems and ultimately alter the hydrologic conditions of the treatment zones such that no further treatment is possible. The capacity to remove nitrogen gas is limited by the ability of water to dissolve nitrogen. Thus, nitrogen present in the feed water will be removed by

stripping with helium gas. Similarly, under methanogenic conditions, methane could be produced in excess of its solubility, causing the same clogging effect as excess nitrogen gas. Thus, methane will also be removed from the feed stream by helium gas stripping.

Removal of Electron Acceptor Demand
Biodegradable compounds such as BTEX, other aromatics and acidic intermediates present in the feed stream diminish the capacity of the feed to remove contaminants from the treatment zone. Thus, to maximize the overall efficiency of the system, i.e., to increase the capacity of the feed stream to mineralize contaminants, the water will be passed though a GAC column prior to augmentation and reinjection. Similarly, hydrogen sulfide will be removed from the feed stream since it may cause a nitrate demand by chemolithotrophs.

(ii) Contaminant Retardation

The advantages of bioremediation may become inconsequential if the overall degradation rate is controlled by slow dissolution, dispersion and/or desorption. Sorption and desorption will be addressed in related laboratory studies. Preliminary experiments done in this laboratory have indicated that BTEX compounds sorb only weakly onto Seal Beach sediments.

(iii) Advection and Dispersion

Advection and dispersion will be predicted based on previous field measurements and best-guess estimates. A transport model will be calibrated using the data developed as part of this demonstration.

(iv) Site Specific Source- or Sink-Processes

Volatilization into the unsaturated zone and dissolution of NAPLs are potential sink and source terms, respectively. To minimize these factors, the treatment zones will be established outside the most heavily contaminated areas and below the water table.

I.C. Demonstration Schedule

divided into the following three phases.

Phase One: 1/1/96-11/31/96. Phase One will last approximately 10 months and will involve development of the hydraulic flow field, the analytical facilities and calibration of the hydraulic model.

Phase Two: 9/1/96-9/1/98. Phase Two will last 24 months and is the duration allotted for the field demonstration and the optimization and evaluation of the anaerobic treatment processes.

Phase Three: 9/1/98-12/31/98. During Phase Three the cost data will be evaluated, reports written, and a technology transfer package with videos and manuals will be developed.

A detailed schedule of activities is indicated below. The demonstration participants are indicated in Appendix A.

II. PREDEMONSTRATION ACTIVITIES

II.A. Selecting the Site

The site selected for this demonstration is a gasoline-contaminated site located on the premises of the Seal Beach Naval Weapons Station, near the intersection of Kitts Highway and Industrial Road. Gasoline contamination at this site was discovered in 1984 when the the old 12,000 gallon steel tank was replaced with a new fiberglass gasoline storage tank. It is estimated that 5,800 gal of gasoline were released into the subsurface. The area has been studied by the U.S. Geological Survey (USGS), Orange County Water District and Stanford University. The Seal Beach site location and the extent of the existing plume, as determined by the USGS, is presented in Figure 1. The site features several characteristics which make it especially well-suited for the demonstration:

(1) The site has been anaerobic for at least a decade. Both laboratory and field studies have demonstrated the presence of anaerobic bacteria that are capable of degrading fuel derived hydrocarbons.

(2) The aquifer is shallow and the cost of placing wells is relatively low.

(3) The regional ground water velocity is low which allows for better control of the hydrogeological geochemical conditions.

(4) The aquifer solids are sufficiently permeable to allow pumping of at least a few gallons per minute, i.e. transmissivity in excess of 2 ft^2 /d. The interbedding of clay lenses within silty sand (possibly sandy silt) are typical for alluvial deposits along the California coast.

(5) The regulatory agency, the CRWQCB, has been supporting the research at the site for many years, including the controlled release experiments. Controlled releases are possible for the verification of removals and mass balance verification.

Conclusions from Previous Field and Laboratory Studies

A summary of previous reports related to Seal Beach project is given in Table 1. The focus in most cases was on anaerobic degradation.

II.B. Selection of Confirmation Laboratory

The demonstration will utilize automated on-line sampling and analysis for the majority of the field samples collected. Additional samples will be collected for the analysis of transformation by-products and the analysis of these samples will be performed at Stanford University utilizing specialized extraction methods developed in-house for the GC/MS analysis of these unique compounds.

II.C. Selection of Analytical Methods

The automated on-line and analysis system will use an Analytic and Remedial Technology, Inc. (A+RT) Automated Sampling and Analysis Platform (ASAP) to collect and process the samples. The ASAP utilizes a modified purge-and-trap system to prepare samples for GC analysis. The GC detectors used will be a photo-ionization detector (PID) in series to a flame ionization detector (FID). The PID and the FID detectora measure the aromatic and aliphatic hydrocarbon contaminants, respectively.

The ASAP will also prepare samples for analysis by a direct reading anion chromatography to measure the electron acceptors and the bromide tracer. The results from a pH probe and a dissolved oxygen probe will be collected as well. All data is automatically stored in a data base which can be retrieved remotely via a modem hookup to the on-site computer. Although the modified purge-and-trap system is not of the design used in standard methods, it has been successfully evaluated through the EPA Site program (EPA/600/R-93/109).

Selected samples will be analyzed for metabolites using procedures developed by Beller er al. 1995.

II.D. Predemonstration Sampling and Analysis

After the installation of the well field and the automated on-line analytical system, samples will be collected from throughout the field site and analyzed. These samples will determine more precisely the extent of the existing contamination and the upper and lower boundaries of the contaminant plume. They will also be used as a part of the demonstration to indicate the extent to which intrinsic bioremediation affects the contaminant concentrations. It is anticipated that some of the wells may not experience a change in electron acceptor concentration for six to eight months.

III. TECHNOLOGY DESCRIPTION

The technology to be evaluated involves the anaerobic destruction (mineralization) of BTEX compounds by augmenting the ground water with mixtures of specific alternative electron acceptors. At the Seal Beach site where the regional ground water flow is very slow, the technology requires bringing the ground water to the surface for treatment and chemical augmentation followed by reinjection to inundate the contaminated zone. Above-ground treatment will involve:

(1) Removal of organic substrates (BTEX and other aromatic hydrocarbons) which limit the capacity of the feed stream to supply electron acceptors;

(2) Removal of nitrogen and methane gas which limit the capacity of the recirculating water to remove mineralization the products; and,

(3) Augmentation of the feed with electron acceptor(s).

To demonstrate the technology for a range of conditions, the above-ground treatment will involve the removal of other electron acceptors through the use of an anion exchange column.

III.A. Technology Application

The technology to be demonstrated involves the use of alternative electron acceptors (other than oxygen) for the in situ bioremediation of ground water contaminated with hydrocarbon fuels. Hydrocarbon contamination most often results from leaking storage tanks or fuel lines and sometimes surface spills which have percolated through the vadose zone to the water table. The focus of the demonstration will be on the BTEX compounds (benzene, toluene, ethylbenzene and the xylene isomers) which are of greatest regulatory concern. Additional aromatic and aliphatic compounds such as other alkylbenzenes, naphthalene and methylnaphthalene isomers will be monitored to the extent feasible.

This demonstration will show the utility of inducing three different electron-accepting conditions, nitrate-reducing and sulfate-reducing and fermentative/methanogenic conditions for removing BTEX compounds from a contaminated aquifer. The technology will demonstrate the efficiency of bioremediation when using alternative electron acceptors and the rates at which degradation can be anticipated under field conditions.

III.B. Advantages and Limitations of the Technology

The main advantage to in situ bioremediation, both aerobic and anaerobic, over conventional pump-and-treat applications are:

(1) Contaminants are mineralized in situ thereby avoiding the physical removal of the solids laden with toxic contaminants and treating large volumes of water in pump-and-treat applications.

(2) In situ bioremediation produces no or only low volumes of secondary waste streams that need to be treated and disposed of; and,

(3) By maintaining a low contaminant concentration in the ground water, the rate of contaminant desorption from the solids is maximized, leading to shorter overall cleanup times.

The advantages of anaerobic bioremediation over aerobic bioremediation are:

(1) Alternate electron acceptors (except ferric iron) are more water soluble and consequently require lower volumes of electron acceptor solution to be supplied to the contaminated zone;

(2) Anaerobic bacteria produce less biomass than aerobic bacteria, and therefore are expected to cause less plugging problems;

(3) The use of anaerobic bioremediation takes advantage of intrinsic processes which occur naturally without intervention, i.e., pumping and treating ground water; and

(4) Factors one through three should result in considerable cost savings over both conventional pump-and-treat and aerobic bioremediation.

The challenges in the application of alternate electron acceptors are:

(1) The process is poorly understood and cleanup times are difficult to predict;

(2) Because there is little operational experience with anaerobic bioremediation, the process is not generally considered acceptable by the regulatory community; and,

(3) Benzene, the compound of greatest regulatory concern, does not appear to be degraded nitrate-reducing conditions and only very slowly under sulfate-reducing conditions.

IV. DEMONSTRATION SITE DESCRIPTION

IV.A. Location

The site for this demonstration is located on the Seal Beach Naval Weapons Station in Southern California. The Seal Beach Naval Weapons Station is located on the transition of a geologic formations called Landing Hill and the Sunset Gap and contains the Seal Beach National Wildlife Refuge, a wetlands marsh. The Wildlife Refuge is in the Sunset Gap. The Sunset Gap is a structural downwarp (Schroeder, 1991):

> Deposits have accumulated on the surface of the downwarp in the Sunset Gap, during the Holocene Epoch, to a thickness of about 30 to 35 feet. These shallow deposits were transported by floodwaters from streams that normally discharged through adjacent gaps, by flow in temporary channels, and by wave action resulting from high-intensity storms. Flood flow now is largely controlled by levees and flood-control channels. The sediments that compose the shallow deposits contain minor amounts of gravel, but particle size generally ranges from clay to coarse sand. Much of this material has been reworked by tides and floods, resulting in interfingering lenses of sand, silt, and clay; thus, correlation of lithologic units can be made only for very short distances.

IV.B. Site History

The contaminated area is underneath a gasoline station located along Kitts Highway. An estimated 5,800 gallons of gasoline leaked from a steel underground storage tank (Figure 1). This tank was removed in 1984 and replaced with a pair of fiberglass tanks.. The most complete site investigation is from Schroeder (1991).

Extent of contamination is as documented in the Schroeder Report (1991) evident from Figure 1. Concentrations at various observation wells have been monitored by the Orange County Water District. Based on data collected in May 1996, the pume has since retracted and is now concentrated around the immediate tank area.

IV.C. Site Characteristics

The flow through well field will be placed in the triangular area east of the railroad tracks near the gas station, Figure 1. This location is closest, non-paved area to the original source of the BTEX contamination. A grab sample taken in June 1995 from Well 2, located within this area, produced the following concentrations for the individual BTEX components: 14.1 mg/L benzene, 13.9 mg/L toluene, 2.7 mg/L ethylbenzene, 8.3 mg/L m,p-xylene, 4.5 mg/L o-xylene. Since this well was not purged before the grab sample was collected, it is anticipated that these concentrations are low. The nitrate concentration was below the detection limit and the sulfate concentration was 2.2 mg/L. Wells located less than 100 feet away typically have approximately 80 mg/L sulfate. Thus, as a demonstration site, these concentrations are environmentally significant and a successful in situ biodegradation demonstration in this location would contribute significantly to the remediation of this contamination.

The stratigraphy in the test zone has been determined from the cores obtained during the well field installation on June 14, 96. Figure 2 shows the location of the wells. The fence diagrams are indicated in Figures 3 and 5. A sand sample has been characterized (Appendix D).

The natural ground water velocity in the vicinity is low, approximately 0.7 cm/day, based upon the modeling results for the slug test demonstrations previously performed.

Hydraulic conductivity, transmissivity and water permeability have not been determined for the test zone and will be determined as part of Phase I of the demonstration: hydraulic characterization of the demonstration field site. During well development of the slug test field site and subsequent pumping, the better wells were able to sustain flow rates of 2 gallons per minute or about twice the anticipated flow rates for this demonstration.

IV.D. Site Maps

A site map is depicted in Figure 1. Additional maps and cross sections have been given by Schroeder (1991).

V. TECHNICAL PERFORMANCE CRITERIA

The main focus of this demonstration is the use of alternative electron acceptors for in situ bioremediation of hydrocarbon fuel contaminants. The proposed design essentially uses an injection/extraction well doublet, where the extraction well is used to create a gradient and supply ground water which will then be augmented above ground with appropriate alternative electron acceptors before being reinjected into an injection well located spatially up gradient. (The details are presented later in the experimental design.)

The performance criteria will be the historical change in contaminant concentrations as measured in the monitoring wells located between the injection and extraction wells. The additional measurement of the concentrations of the alternative electron acceptors and by-products formed will further validate the degradation of the contaminants. Further validation can be obtained through the controlled release of known masses of the BTEX compounds.

V.A. Contaminants

The target contaminants include benzene, toluene, ethylbenzene and the o-, m- and p-xylene isomers (BTEX) compounds. Other aromatic and aliphatic hydrocarbon compounds typically present in hydrocarbon fuels will also be analyzed and studied to whatever extent is feasible. The maximum contaminant limits for the various BTEX compounds are listed in Table 2 below.

Table 2. Maximum Contaminant Limit for BTEX Compounds

Contaminant	MCL
Benzene	5 µg/L
Toluene	1000 ~~40~~ µg/L
Ethylbenzene	700 ~~30~~ µg/L
Xylene	10,000 ~~20~~ µg/L

National Secondary Drinking Water Regulations (Journal AWWA, Feb. 1990, pp. 32-52)

V.B. Process Waste

Depending on the treatment conditions, the extracted water may contain compounds that are undesirable, including hydrogen sulfide, BTEX, and/or methane. In order to reuse the extracted water as feed water, these constituents must be removed. For this demonstration, we also will remove excess electron acceptor using an anion exchange process. The brine produced from regenerating the anion exchange columns will need to be disposed of. It is anticipated that this waste stream can be disposed of through the sanitary sewer system. The extracted ground water will be treated with GAC to remove the hydrocarbon fuel contaminants prior to reinjection into the subsurface environment. The spent GAC represents a waste stream which must also be disposed of, preferably by regeneration.

In addition, the analytical system used and the injection system will also produce a waste stream of less than 500 ml/min. This water stream would not normally be produced in a the typical application of the technology because it is directly related to sampling for the evaluation of the

treatment methodology. This waste stream will be discharged to the extraction well and thus will essentially recirculate within the system.

V.C. Reliability

Anaerobic bioremediation is an emerging technology and insufficient data exists to predict it's reliability. The reliability of anaerobic bioremediation will depend on:

(1) The presence and viability of anaerobic bacteria capable of growing on BTEX compounds. Growth depends on the ability of maintaining an adequate supply of electron acceptors in the aquifer and removing reduced and inhibiting products. Supply of electron acceptors and removal of interfering products is assured by recirculating and treating the water as indicated above. For the treatment to proceed, recirculation does not need to be continuous. Therefore, a temporary shutdown of the recirculation system would not cause any damage to the treatment process.

(2) The reliability of the hardware used for recirculating water through the treatment zone. Such hardware is commercially available. Using the injection/extraction well doublet design: a variable speed submergible pump is used in the extraction well to create the flow stream to the injection well. A controlled flow rate spike addition of the alternative electron acceptor is all that is required for operation. A simple pressure switch, motor contactor relay and solenoid valve should be incorporated to prevent election acceptor spike addition in case of extraction well pump failure. Mixing is accomplished with an in-line static mixer. In the case where it is necessary to remove undesirable electron acceptors, a standard home type water softener (or two) utilizing an anion exchange resin would be inserted into the flow path before the alternative electron acceptor spike stream; initial adjustment would require monitoring effluent anion water quality.

Potential problems in the application of anaerobic bioremediation technology are:

1. Injection well plugging: During the operation of the remediation system plugging of the well sand pack of the injection wells may occur. This should be considerably less than would be encountered with aerobic in situ bioremediation since the biomass yield is lower for anaerobic bacteria. Plugging of the sand pack could be controlled by the daily addition of a pulse of 0.1% hydrogen peroxide with a duration of one to two hours. This would not be sufficient to significantly increase the aerobic population around the well screen sand pack but would be detrimental to the anaerobic biomass in the sand pack. This process will not be used during this demonstration unless the injection well head pressure starts to increase significantly, since it will distort the performance evaluation of the alternative electron acceptors.

2. Plugging of the aquifer in the treatment zone: Plugging of the treatment zone will be avoided by limiting the concentrations of the aquifer. Plugging of the treatment zone due to biological growth or chemical precipitation is not likely in aquifers having a transmissivity in excess of 2 ft^2/d.

3. Toxic by-product formation: By-product toxicity or inhibition of microbial activity could have significant impact on the reliability of the microbial process. For example, the production of hydrogen sulfide may inhibit the hydrocarbon degradation at very low concentration levels.

4. Limiting nutrients: Some nutrients, such as phosphate or ammonium, may become limiting. Changes in available minor nutrient concentration, e.g. phosphate or nitrogen, may change the effectiveness of the biological processes.

5. Excessive gas formation: If nitrate is used as the alternative electron acceptor, for each mole of contaminant biodegraded, 3.6 moles of nitrogen gas is produced. Nitrogen gas has a solubility in water of about 20 mg/L at 20 °C. Thus, nitrogen saturation of the bulk ground water will occur when the equivalent of 18 mg/L toluene of the hydrocarbon fuel contaminates are degraded. If the ground water is already at air saturation (approximately 80% nitrogen), only 3.6 mg/L of the hydrocarbon contaminant degradation would result in saturation of the bulk ground water. This problem may be more pronounced in the smaller pore structures of the aquifer where the hydrocarbon contaminants tend to accumulate and when degraded, produce nitrogen gas bubbles which plug the pore structure and thus block dispersion of the nitrate and/or diffusion of the hydrocarbon contaminant.

V.D. Ease of Use

A precondition for the application of the technology is knowing the biological and chemical factors which affect anaerobic biotransformation of fuel hydrocarbons. In addition, it is necessary to know in detail the hydrogeologic conditions of the site, the contaminant distribution, and the water quality. Application of the technology will depend on the specific conditions of the site. Under certain favorable conditions, the supply of electron acceptors to the contaminated zone through the natural flow of ground water will be sufficient to maintain the biological oxidation process.

At sites where ground water flow is slow (such as the Seal Beach site), the supply of electron acceptors and the removal of reduced products will be rate limiting. Under these conditions, it may be necessary to supply the ground water with additional electron acceptor(s) by inducing a recirculating flow and treating the water prior to injection. Supplying a contaminated zone with electron acceptor(s) and removing reduced products may involve the following operations:

(1) Maintaining a specific concentration of alternative electron acceptors in the feed water stream,

(2) Treating the feedwater such that no contaminants are introduced into the ground; and,

(3) Maintaining hydrologic conditions for optimal control of the process.

All three operations are standard, and appropriate hardware is available from commercial suppliers. Operational training should be minimal, OSHA 40 hr hazardous materials training should be required and the individual should be trained to work with the specific chemicals used.

V.E. Versatility

The technology may be applicable to other contaminant groups which are degraded under specific redox conditions.

V.F. Off-the-Shelf Procurement

The technology to be demonstrated is emerging and not available as a standard procedure. However, individual hardware components detailed below are used commonly and are available commercially. Software which may later be used for process control will be developed as part of this project.

V.G. Maintenance

Maintaining a site-cleanup operation will entail the following tasks:

(1) Maintaining the extraction and injections flows. The type of pump selected for the electron acceptor spike will affect maintenance and this selection is dependent upon the extraction well flow rate involved. Submergible pumps generally do not require much maintenance as long as they are not left down hole without being used for extended periods of time.

(2) Monitoring water quality in feed stream, ground water monitoring wells, and water treatment system.

(3) Maintaining the water treatment system. This involves replacing GAC and providing sodium chloride for anion exchange resin regeneration.

(4) Ensuring a constant supply of electron acceptor feed solution. On a regular basis, fresh electron acceptor feed solution will be prepared using clean tap water and salts. Biological growth in the feed solution should not be a problem at the high concentrations used.

V.H. Scale-up Issues

The scale of this demonstration will allow extrapolation to larger scale sites. The most critical issues relate to the hydraulic control which depend on the hydrogeologic conditions. As the treatment zones are increased in size, the time period necessary for affecting the geochemical conditions will get longer. To accelerate and to gain better control of the process, more wells may have to be installed which would increase the costs.

Scaling up by increasing the number of wells may have little impact on the other components used for the remediation since the augmentation of the alternative electron acceptor may be continuous and the equipment for the augmentation can be moved from well to well as needed. The wells not being used for augmentation can be used to monitor the alternative electron acceptor concentration and the progress of the remediation.

VI. COST PERFORMANCE DATA

This section indicates standard terminology for site classification, the expected parameters affecting cost performance, and methodology to be used for validating the expected operational costs of enhanced in situ bioremediation. The basic methodology has been outlined in the "Guide to Documenting Cost and Performance for Remediation Projects," Member Agencies of the Federal Remediation Roundtable, EPA-542-B-95-002, March 95.

VI.A. Standard Terminology

The site will be classified using the terminology indicated in Table 3. It is a liquid underground fuel site with BTEX compounds as the principal contaminants. The treament technology entails stimulation of intrinsic biological oxidation with alternate electron acceptors and fermentation. The electron acceptor feedstream will be pretreated using activated carbon and deionization.

Table 3. Standard Terminology

Site Background
Historical Activity that Generated Contamination
Leaking Underground Gasoline Storage Tank, (Hydrocarbons, benzene, toluene, ethylbenzene, and xylenes)

Site Characteristics
Media Treated
Groundwater and soil (in situ)

Contaminants Treated
BTEX, total hydrocarbons

Treatment System
Primary Treatment Technology
biological oxidation using alternate electron acceptors and fermentation

Supplemental Technology
Pretreatment Feed Water - activated carbon, deionization, nitrate and sulfate amendment

VI.B. Parameters Affecting Cost or Performance

Technology cost or perfomance is affected by waste characteristics and treatment technology operating conditions. Tables 4 and 5 list matrix characteristics and operating conditions, respectively, expected to affect performance or costs.

Table 4. Matrix Characteristics Expected to Affect Treatment Cost or Performance

Soil Properties	Value	Method
Soil Classification		
Clay Content and/or Particle Size Distribution		
Sorption		
Biomass Concentration		
Hydrogeologic Properties		
Groundwater Velocity		
Hydraulic Conductivity		
Porosity		
pH		
Water Quality		
Waste Properties		
Total Organic Carbon		
Biodegradable Organic Carbon		
Nonaqueous Liquids		
BTEX Concentration		

Table 5. Operating Parameters Expected to Affect Treatment Cost or Performance

System Parameters	Value	Measurement Procedure
Feed Water Volume		
pH		
Nitrate and Sulfate Concentrations		

VI.C Work Breakdown and Cost Elements

Cost elements are grouped by when the activity occurs -- before, during or after treatment. The cost elements for a second-level breakdown structure is indicated in Table 6.

Table 6. Work Breakdown Structure Cost Elements (Second Level for Before and after Treatment, Fifth Level for Treatment Costs)

Inter Agency WBS#	Cost Element	Unit Cost ($)	No. of Units	Cost ($)
Before Treatment	Labor		area	
	Planning & contracting		area	
	Permitting & regulatory requirements		lump sum	
	Site Preparation - Well Installation - Site Characterization		area	
	Capital Equipment - treatment system		area	
	Construction		area	
Treatment year 1	- Labor - Monitoring (sampling) - Analytical Services (sampling) - Equipment or facility modification - Effluent treatment and disposal (DI brine) - Residual waste handling and disposal (activated carbon, - Ancilliary equipment - Consumables and supplies (electron acceptors, power)		area area area area area area site area	
yr 2				
After treatment	Removal of equipment and structures		area	
	Site restoration		area	
	Decontamination		area	
	Demobilization		area	

The number of years treatment will be needed will increase with the mass of fuel hydrocarbons.

The expected costs associated with the initial well installation and well development costs are detailed in Appendix B.

Using nitrate as the alternative electron acceptor, 4.8 mg of nitrate are required to biologically degrade 1 mg of hydrocarbon fuel contaminant (as toluene). To oxidize one kg of fuel, 4.8 kg of nitrate are needed. Assuming the cost of potassium nitrate to be $23/kg, it would cost approximately $100 to oxidize 1 kg of fuel ignoring all other costs.

VII. SAMPLING PLAN TO ADDRESS PERFORMANCE CRITERIA

VII.A. Overview of Sampling Operations

This demonstration will evaluate three different treatments simultaneously and considerable effort will be placed on the sampling and analysis process. The demonstration will utilize automated on-line sampling and analysis for the majority of the field samples collected.
The automated system will process field samples using:

- purge-and-trap GC analysis for the hydrocarbon fuel contaminants,
- ion chromatography for the electron acceptors and conservative tracer,
- probes for pH and dissolved oxygen analysis.

Some samples will also be manually collected from outlying wells which are not connected to the automated system. These samples will be used to evaluate intrinsic biodegradation and will be analyzed by the automated system in the off-line mode. A more detailed description of the automated sampling system is given in Appendix A, Quality Assurance Plan, Section 2.2.2.4.

Additional samples will be collected for the analysis of transformation by-products and the analysis of these samples will be performed at Stanford University utilizing specialized extraction methods developed in-house for the GC/MS analysis of these unique compounds as described in Beller et al. (1995). Samples will also be collected for analysis of general parameters such as TOC.

VII.B. Documentation, Logistics and Equipment

The automated system is self calibrating, except for the probes, and maintains separated data bases for

1) Field data results including off-line samples,

2) Blank and quality control check samples, and

3) Detector response factors from generated calibration samples.

All samples are will be stamped with date and time and have unique names for sample locations. Samples collected manually will be logged into the field site notebook and, after shipping to Stanford University, will also be logged into a master project sample notebook. Samples shipped to the confirmatory laboratory will also be logged into the field site notebook; shipping documents will be attached to the chain-of-custody.

VII.C. Sample Collection Procedures

As previously described, an automated on-line sampling and analysis system will be utilized. The automated on-line sampling manifold will have 111 sample ports, of which 105 ports will be connected directly the multilevel sample bundles used for monitoring wells via 3/16" stainless steel sample lines. The remaining six ports will be connected to the treatment system and the three injection wells. Sample waste water will recycled back to the extraction well.

The internal volume of 3/16" tubing is approximately 2.5 ml/foot. Assuming the longest sample line, including the sample bundle, to be 20 meters, the internal volume of the stainless steel tube would be 165 ml. Using ten flush volumes to ensure a representative sample, and assuming an

aquifer porosity of 0.3, the flush volume would occupy a sphere of having 8.6 inch diameter. With the spacing of the sample points at 14" apart, each sample point will represent a discretely different location.

With an anticipated sample cycle of 45 minutes, to completely sample and analyze all samples within the field would take about four days, including QA/QC samples. As such, results from some sample locations may be determined to be of lessor value during various phases of the demonstration and therefore sampled less frequently, conversely, other locations may be found to have greater priority and therefore sampled more frequently. For example, during the injection process, certain samples locations will be selected for more frequent sampling in order to observe breakthrough of the conservative tracer and relative retardation of the BTEX compounds. The automated sampling system is expected to be in operation essentially continuously during the demonstration processing nearly 1000 sample per month.

Off-line samples will be collected utilizing a custom built sampling manifold where samples are collected in a head space free manor. The wetted materials of the sampling manifold are stainless steel, glass and Viton® o-rings. Considering the 105 available sample locations and the time involved in processing each sample, careful consideration needs to be placed upon the frequency and location of samples collected for metabolite analysis. A metabolite sampling plan will be amended to the work plan at a later date.

VII.C.i. Sampling Locations and Well Design

The well field is described in VIII.C "Ground Water Flow Field And Sampling Design". Each of the three injection well creating the three treatment zones will have five associated multilevel sample wells. For each zone, one multilevel sample well will be located approximately 7 meters upgradient of the injection well and two multilevel sample wells well be located two and four meters in the direction of the extraction well. For two of the treatment zones, an additional two multilevel sample wells will be located approximately in the direction of the natural gradient, two and four meters from the injection well. For the treatment zone upgradient from the extraction well, the two remaining multilevel sample wells will be placed 6 and 8 meters downgradient continuing the line in the direction of the extraction well, Figure 2.

The multilevel sample wells will be composed of a bundle of seven, 3/16" stainless steel tubes with the lower end of each tube spaced at 14" intervals, thus providing seven discrete sample locations covering the length of the injection well screens at each monitoring well location. The end of each sample tube be enclosed in glass wool filter protected by nylon "horse hair" fabric, a double weave knit. The sample bundle will be placed within a 2" borehole, backfilled with sand, thus minimizing required flush volumes to obtain representative samples.

VII.C.ii. Soil or Other Sampling Procedures

During the drilling process, core samples will be collected continuously from the injection wells and the extraction wells. These will be collected using a California split spoon sampler and the brass liners will be sterilized prior to use. Core will be refrigerated as soon as possible, but probably not before being returned to Stanford University. If possible, cores will also be collected from the monitoring wells.

VII.C.iii. Sample Storage, Packing and Shipping

Water samples will be collected using pre-cleaned bottles and where appropriate, preservatives will be added to maintain the integrity of the sample. The size of the bottle and the preservative, if any, will be noted in the field notebook. Samples will be refrigerated before packaging for shipping. Packaging for shipping will include frozen Blue Ice® containers to keep samples cool during shipping, and packaging container will be ice chests with positive latching lids. Shipping is to be by Federal Express, overnight priority, and will be limited to Mondays through Thursdays.

VII.C.iv. Decontamination Schedule

The sampling manifold will be decontaminated between sample locations and at the end of the sampling session using deionized water only.

VIIC.v. Analytes of Interest for Field Samples Collected On-Line

The ASAP system is designed to automatically collect samples from a number of descrete sample locations and process sample aliquots by various techniques for specific analytes. The hydrocarbon fuel contaminants will be analyzed by purge-and-trap GC, electron acceptors and conservative tracer will be analyzed by ion chromatography, and the system utilizes probes for pH and dissolved oxygen analysis.

The GC column utilized will be a 30 meter DB-Wax which will resolve m-xylene and p-xylene. The GC will also utilize tandum photo and flame ionization detectors, thus providing detection of both the aromatic and aliphatic compounds. Utilizing a post column switching valve to a second column, a GasPro GCG column connected to a pulsed helium ionization detector, PHID, the GC may also resolve and detect gases such as oxygen, nitrogen and methane. Table 7 summarizes the compounds to be measured on-line and the intruments to be used.

Table 7. Compounds Analyzed by the Automated Sampling System

Compound	GC	IC	Probe
Methane	X		
Butane	X		
Pentane	X		
Hexane	X		
Benzene	X		
Toluene	X		
Ethylbenzene	X		
Xylenes	X		
Trimethylbenzenes	X		
Chloride		X	
Bromide		X	
Nitrate		X	
Sulfate		X	
Dissolved Oxygen	X		X
Dissolved Nitrogen	X		
pH			X

VIII. EXPERIMETAL DESIGN

VIII.A. Objectives

The principal objective is to demonstrate the utility of enhanced intrinsic bioremediation for the clean-up of sites contaminated by hydrocarbon fuels. Specific objectives are to:

(1) Determine the capacity of denitrifying, sulfidogenic and methanogenic bacteria to mineralize fuel hydrocarbons under in situ conditions;

(2) Establish the optimal procedure for supplying electron acceptors including nitrate, sulfate and bicarbonate to an anaerobic aquifer contaminated with fuel hydrocarbons;

(3) Demonstrate the utility of biomarkers for assessing hydrocarbon transformation; and,

(4) Evaluate and calibrate a large scale hydrogeologic transport- and reaction model for anaerobic biotransformation of BTEX compounds.

VIII.B. Factors To Be Considered

Some of the factors which are deemed significant are discussed below. Included are the redox conditions expressed as the concentrations of the electron acceptors (oxygen, nitrate, sulfate and bicarbonate), the BTEX concentration, the formation of end-products (nitrogen, H_2S, and methane), the residence time and travel distance, the pH and temperature.

1. Electron acceptor concentration: The electron acceptor concentrations will be controlled by first removing all nitrate and sulfate from the extracted ground water by anion exchange and then augmenting the feed water with appropriate concentrations of oxygen, nitrate, sulfate or bicarbonate as needed.

2. Substrate Concentrations: Two sources of BTEX compounds will be considered: (i) the contaminated aquifer solids which release BTEX into the ground water and (ii) BTEX compounds present in the feed stream. To control the BTEX concentration in the feed, the extracted ground water will be treated with GAC and then amended with BTEX as needed. The simultaneous presence of hydrocarbon compounds affects the removal of individual contaminants.

3. End-product Formation: The metabolic end-products of denitrification, sulfate reduction and methanogenesis are, respectively, N_2, H_2S and CH_4. Their formation will be controlled by limiting the supply of the appropriate electron acceptors. Special consideration will be given to solubility limitation of N2 and CH_4 and inhibition by H_2S, which is toxic to some bacteria.

4: Residence Time: Two pairs of wells and an upgradient well will be installed placed in such a way that the predicted residence time will be approximately 3 and 18 days at the design flow of 1.5 L/min (assuming homogenous aquifer). The rate of injection may be changed to change the residence times.

5. pH: The pH in the aquifer will not be controlled but will be measured regularly. The pH of the feed water will be maintained between 6 and 8.

6. Temperature: The temperature will not be controlled but measured regularly.

7. Retardation: Retardation is affected by sorption and desorption processes which also affect the bioavailability. Laboratory sorption studies have indicated very weak sorption for BTEX compounds.

VIII.C. Ground Water Flow Field And Sampling Design

A mixed recirculation/stopped flow design will be used for treatment evaluations. The proposed design will consist of one common extraction well and three individual injection wells, each of which will be used to create a different treatment zone. Each evaluation will consist of a recirculation phase during which the treatment zones are incubated with water of a defined composition. During the evaluation phase, the flow will be stopped and the contaminant removals will be monitored by analyzing samples collected from the injection and observation wells within the treatment zones. The feed water to the treatment zones will be treated to obtain water of a consistent and defined quality and will be augmented with electron acceptor(s) and BTEX as needed. Recirculation of the water during the controlled release phase will be used to release BTEX into the test zone. A controlled release will last approximately 2 weeks and will establish treatment zones approximately 100 m^3 in size. After a controlled release, the flow will be stopped and the BTEX concentration will be observed as a function of time for up to six months. BTEX concentrations will be measured at four multi-level observation wells with up to six observation points.

Figure 2 shows the location of the extraction well, the three injection wells, the observation wells associated with each injection well. With this design, three different test zones will be created allowing the execution of three parallel demonstrations for the evaluation of three different treatments. The three injection wells will be placed in areas of moderate contamination, while the extraction well will be located in an area of relatively high contamination. For well design see Appendix E.

VIII.D. Treatment Evaluation

The different treatments to be evaluated are summarized in Table 8. The contaminated ground water to be used as the feed will be extracted from the newly installed well 43-1. In this well, we expect that organics concentration is high and that all of the nitrate and a significant fraction of the sulfate has been consumed. The ground water treatment system which will be used in some evaluations to pretreat the feed water streams is depicted in Figure 5. It includes two granulated activated carbon (GAC) columns, two anion exchange columns for electron acceptor removal and a helium stripping column for residual BTEX and oxygen removal. The feeding and augmentation system to be used is shown in Figure 6. It includes gear pumps to provide a controlled flow to the injection wells and the three electron acceptor feed streams.

The schedule of activities is indicated in Figure 7. After installation of the wells, the wells will be tested hydrologically as described below. Then, each treatment zone will be "flushed" with treated, unamended GAC treated ground water to replace the test zone groundwater with water of defined composition. The data collected during the initial flushing will serve to (i) establish baseline data of BTEX concentrations, (ii) determine chloride breakthrough curves at the different monitoring wells, (iii) test the performance of the treatment and analytical systems. Then, to establish the microflora, another slug of water will be injected containing the appropriate electron acceptor mix for the respective test zone. The presence of electron acceptors will will allow the microflora to establish itself. This phase is called "Treatment Zone Establishment." It is expected that during this time, a substantial portion of the existing contamination will be removed.

However, due to the complicated relationships between desorption, degradation and retarded transport, evaluation of these data will be difficult. Therefore, in the subsequent evaluations, each test zone will be inundated with water of known BTEX and electron acceptor concentrations. Prior to a controlled release, the treatment zone will be flushed with ground water to remove any residual tracer which may be present from the treatment zone establishment or one of the previous treatment zone evaluations. Three controlled releases are planned, two with synthetic mixtures of BTEX and one with contaminated ground water containing significant amounts of BTEX. After the controlled releases (which are expected to last for two weeks), the recirculating flow (and therefore the releases) will be stopped. At this stage, the injection well and four observation wells located in each treatment zone will be sampled and analyzed on a regular basis to obtain compound removal data.

A total of three treatment evaluations will be performed for each test zone. Evaluation 1 and 2 will be conducted using similar conditions to verify the findings from each of these evaluations. The first two controlled releases will use synthetic BTEX mixtures, while the third controlled releases (Evaluations 3) will use contaminated ground water. During Evaluations 3 and 4, ground water treatment with GAC will be omitted. However, the contaminated ground water will be treated with anion exchange, augmented with BTEX if needed, and augmented with appropriate mixtures of electron acceptors prior to being injected into the test zones.

Table 8: Overview of Treatment Evaluations

Test Zone	T1	T2	T3
Redox Conditions	- Fermentative/ Methanogenic	- Sulfate-Reducing - Fermentative/ Methanogenic	- Nitrate-Reducing/ - Sulfate-Reducing - Fermentative/ Methanogenic
	Ground Water Amendments During Field Activities		
Flushing	None	None	None
Treatment Zone Establishment	Tracer Bicarbonate	Tracer Sulfate Bicarbonate	Tracer Nitrate Sulfate Bicarbonate
Controlled Releases 1 and 2	Tracer Bicarbonate BTEX	Tracer Sulfate Bicarbonate BTEX	Tracer Nitrate Sulfate Bicarbonate BTEX
Controlled Releases 3 and 4	Tracer Bicarbonate Contaminated Ground Water	Tracer Sulfate Bicarbonate Contaminated Ground Water	Tracer Nitrate Sulfate Bicarbonate Contaminated Ground Water

The feed stream for the three test zones will be treated as follows:

Test Zone T1: The feed for T1 will be treated by GAC to remove organics, passed through an anion exchange column to remove residual electron acceptors and augmented with tracer. In the absence of nitrate and sulfate, we expect methanogenic conditions to develop in the test zone impacted by the feed T1.

Test Zone T2: The feed for T2 will be treated by GAC and then passed through an anion exchange column. The feed will then be augmented with tracer, sulfate and bicarbonate. In T2, we expect to develop sulfidogenic conditions followed by methanogenic conditions.

Test Zone T3: The feed for T3 will be treated by GAC and passed through an anion exchange column, stripped with helium to remove gaseous nitrogen and then augmented with tracer, nitrate, sulfate and bicarbonate. The concentration of nitrate during treatment zone establishment will be 45 mg/L. Then, the nitrate concentration will be adjusted upward or downward as needed. In T3, we expect to develop sequential redox conditions of nitrate-reducing, sulfate-reducing, and finally methanogenic conditions.

BTEX biotransformation will be inferred from the BTEX concentration decrease with time and the formation of characteristic benzylsuccinic acid and related metabolites.

The tentative sampling schedule is indicated in Table 9. The controlled releases will be stacked by two weeks or longer to lower the sampling load.

Table 9. Tentative Sampling Schedule During the Various Activities

ACTIVITY	WELL	SAMPLING SCHEDULE
Flushing	All Wells	Once per week
Treatment Zone Establishment	2 day well 6 day well 18 day well	Once per day until breakthough starting at day 3 Once per day until breakthough starting at day 8 Once per day until breakthough starting at day 8
Contolled Release	2 day well 6 day well 18 day well	Once per day until breakthough starting at day 3 Once per day until breakthough starting at day 8 Once per day until breakthough starting at day 8
Treatment Zone Evaluation	All wells	Twice per week

VIII. E Microbial Metabolites Analyses

Selected groundwater samples each sample bundle will analyzed for semivolatile metabolites using diethyl ether extraction, derivatization with diazomethane (to form methyl esters), and GC/MS analysis (Beller et al. 1995). Briefly, samples for metabolite characterization will be collected in solvent cleaned 1 L bottles and preserved with a few drops of conc. HCl (pH <1). Samples will be shipped to Stanford in ice-cooled containers and stored at 4^{o}C until analysis. Metabolites will be extracted with diethyl ether in 2-L separatory funnels. The extract will be concentrated to 2 ml. Then the metabolites will be derivatized using diazomethane and analyzed with GC/MS.Per controlled release demonstration, we plan to obtain one composite sample from at least one of the observation wells of each test zone. Samples will be taken during rapid BTEX transformation. The target compounds included benzylsuccinic acid related compounds (Figure 8) and other alkybenzoic acids (Beller et al. 1995).

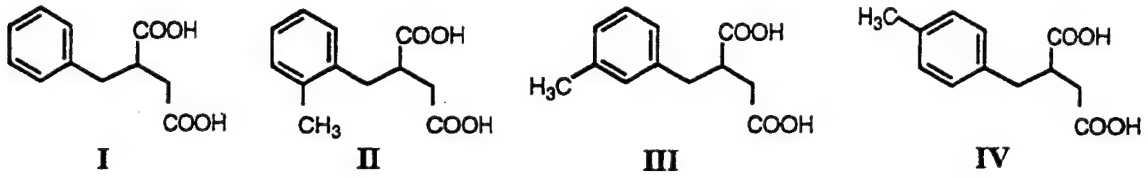

Figure 8. Structures of some of the target compounds for metabolite analysis: I = benzylsuccinic acid, II = (2-methylbenzyl)succinic acid, III = (3-methylbenzyl)succinic acid, and IV = (4-methylbenzyl)succinic acid. These compounds are anaerobic metabolites of toluene, and *o*-, *m*-, and *p*-xylene, respectively (Beller et al. 1995).

VIII.E. Statistical Analysis

Form each observation well, data from the composite tube and six sampling ports will be collected. The variability of the individual sampling ports will be evaluated using standard statistical procedures.

IX. DATA MANAGEMENT AND ANALYSIS

A number of computer models will be used to provide insight into the physical, chemical and biological processes occurring at the site. The modeling effort will be divided into major sections. One set of models will be used to stimulate the flow and transport at the regional scale. This will allow us to predict, in a broad sense, how the entire BTEX plume will evolve over time. Another set of models will be used to simulate in detail the fate and transport of the contaminants in the test zone.

The programs MODFLOW and BIOPLUME II will be used to address the issues of importance at the regional scale. For example, these models will allow us to predict whether the plume is expanding or shrinking with time and at what rate this is occurring. They will also help us understand the natural biological processes occurring within the treatment zone.

Two computer based models are being developed to model the treatment zone in detail. The first of these models is relatively simple and will be used in the planning and design stages of the project. Although this model assumes that the aquifer is homogeneous and neglects dispersion and reactions, it will provide useful information. The model computes the flow field analytically and then uses this flow field to determine solute travel times and the zone of injection influence. Of course, the calculated values are only approximations, but these estimates may be used to guide the placement of the wells and to choose the recirculation flow rates.

Another model that considers multiple-species is being developed to model the treatment zone in much greater detail. This multi-species reactive transport model will be used as the experimental design is completed and we gather more specific information about the effect of treatment. The model simulates the reactive transport of all compounds, the BTEX compounds and the electron acceptor(s), injected and desorbing from the aquifer solids. It will also model the presence of metabolites that are produced biologically. This model will be used to compare the reaction rates in the field with those observed in the laboratory.

As data from the demonstration is gathered, they will be compared with the model results. As more data is taken, the model parameters such as dispersivity and reaction rates will be modified to match the data as well as possible. Probably, the reaction rates observed in the field will differ considerably from the rates observed in the laboratory. The reasons for this discrepancy will be investigated and a relation between the two reaction rates will be sought. Calculating the reaction parameters which match the data will aid in judging the efficiency of the treatment method. This will be done by comparing the reaction rates within the enhanced zone with the rates for the control region.

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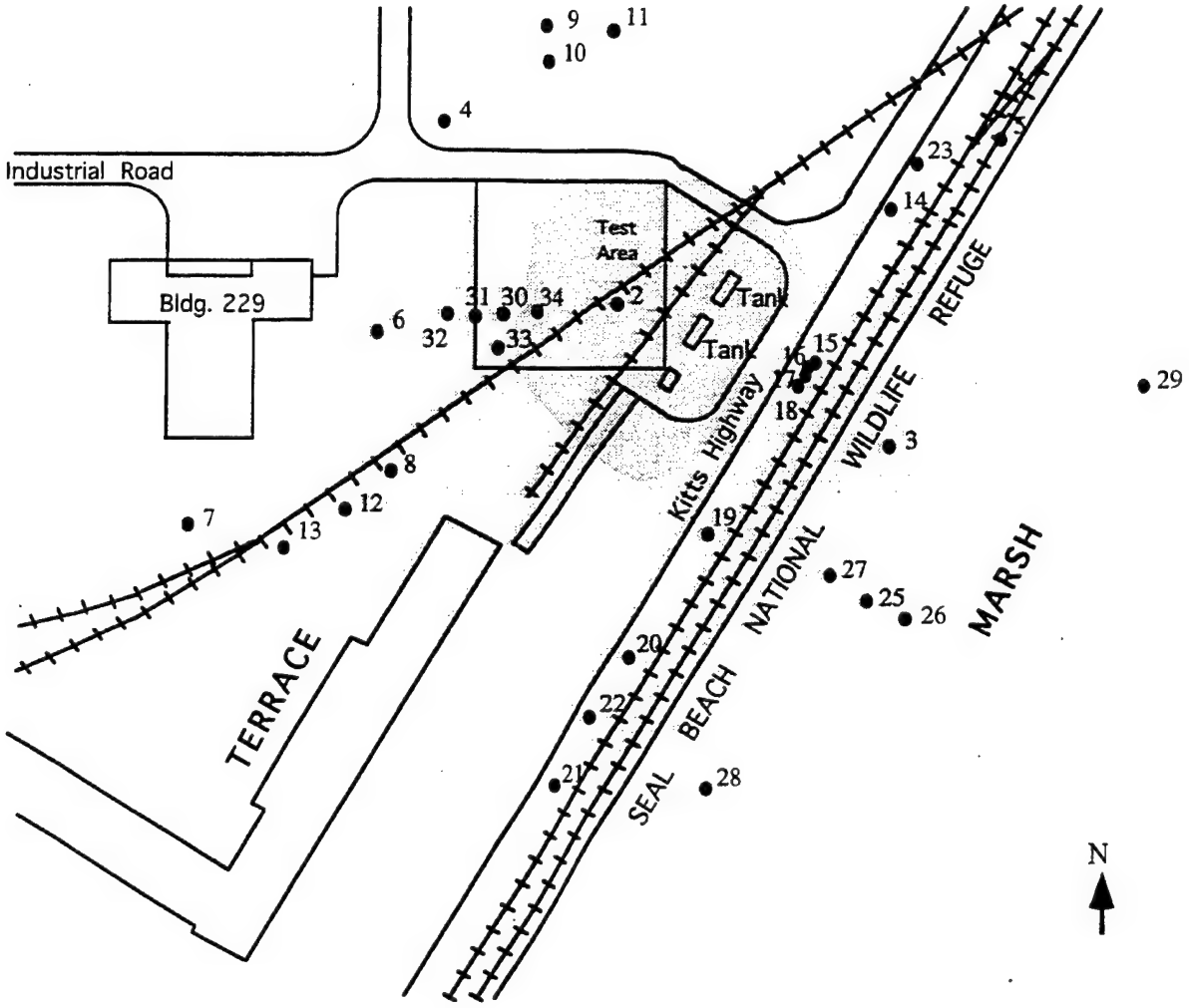
XI. DATE AND SIGNITURE OF PROJECT LEAD

Stanford, California, October 11, 1995

Martin Reinhard.

List of Figures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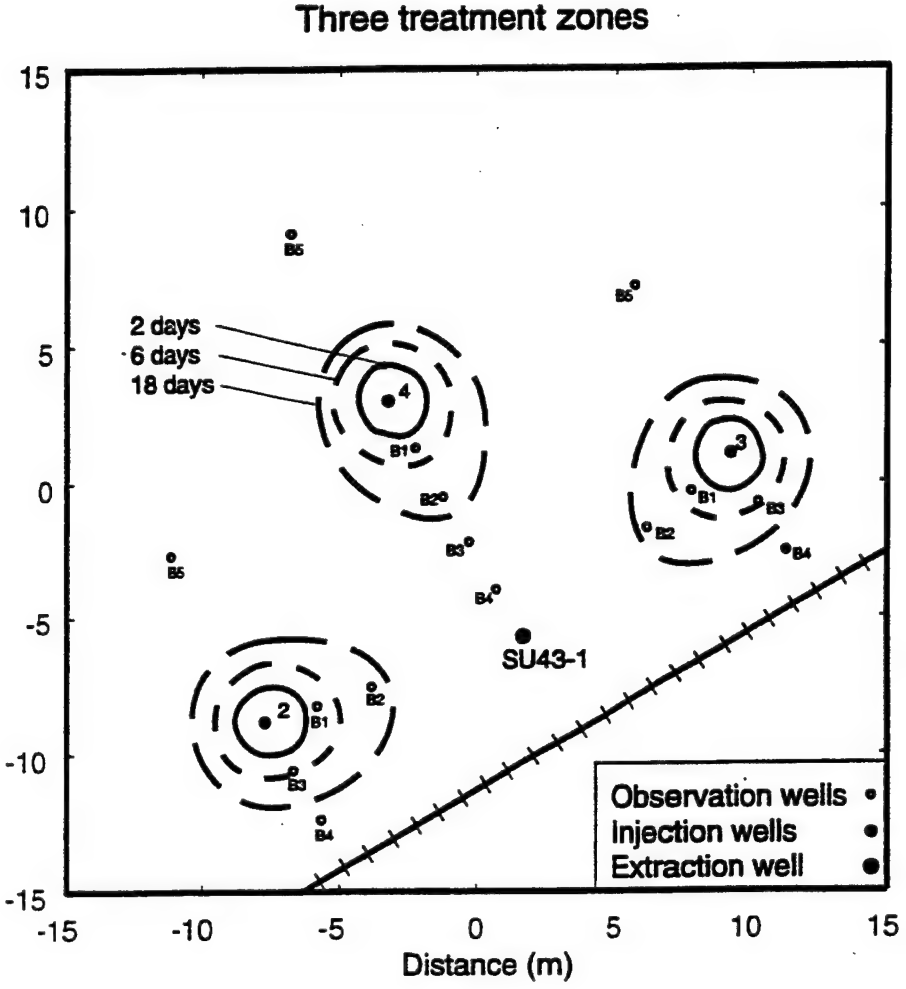
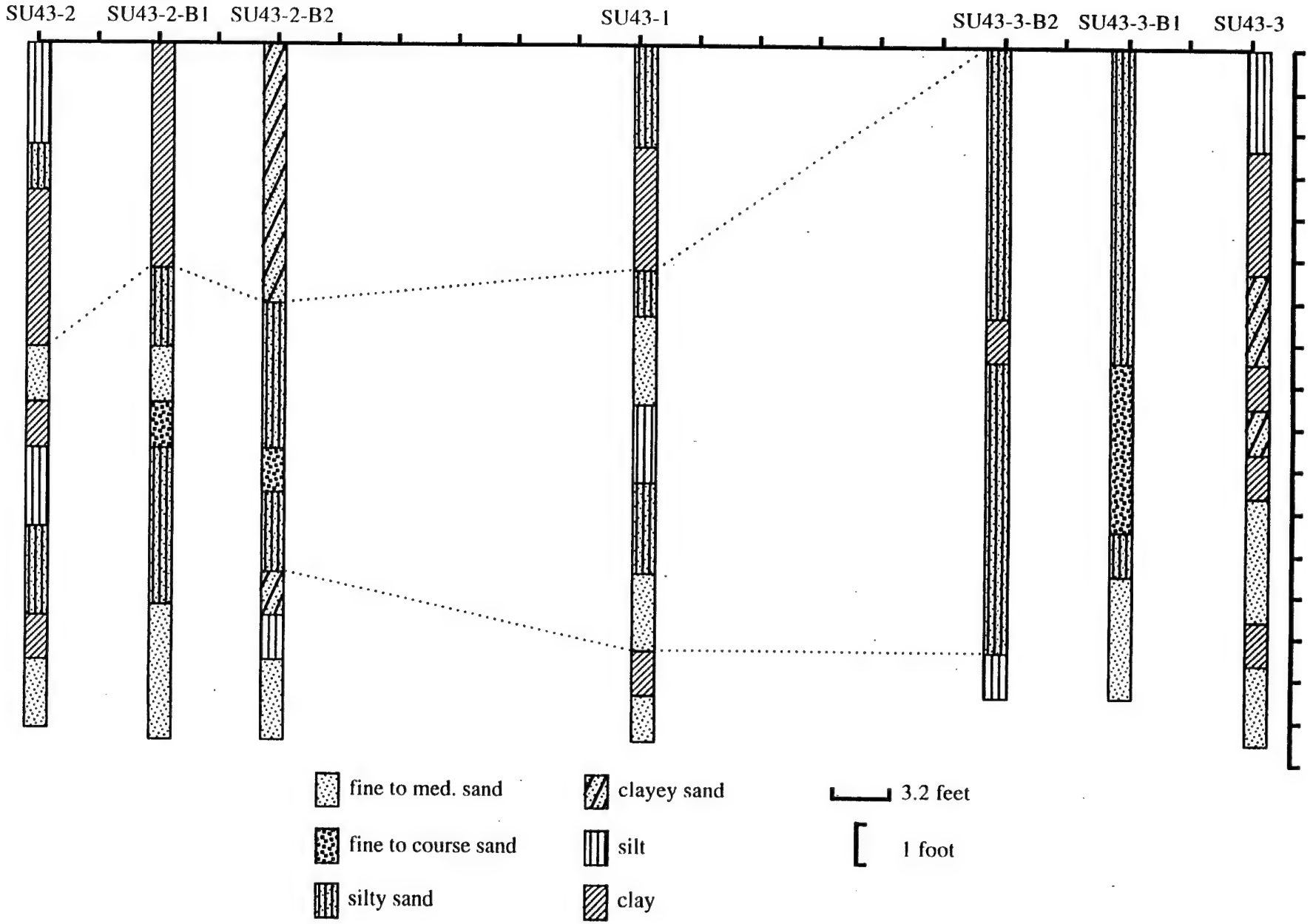
Theoretical Extent of Injection Influence

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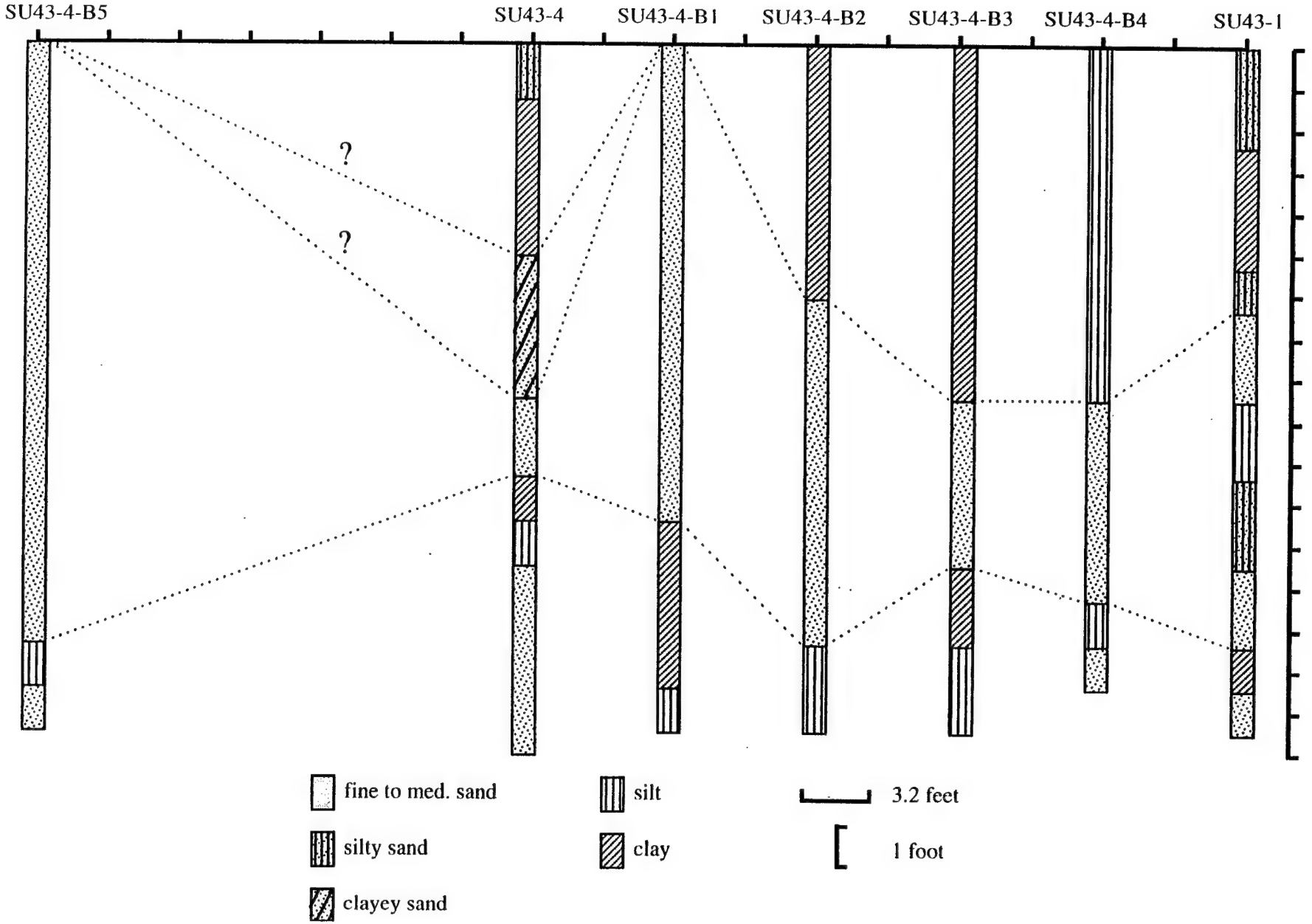
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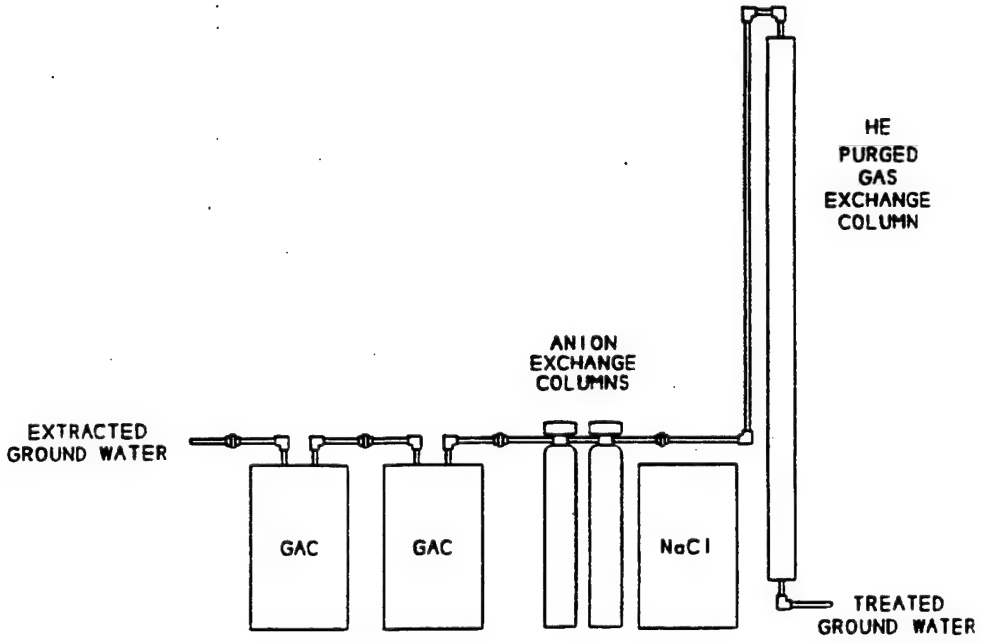

Figure 5. Seal Beach Ground Water Pretreatment System

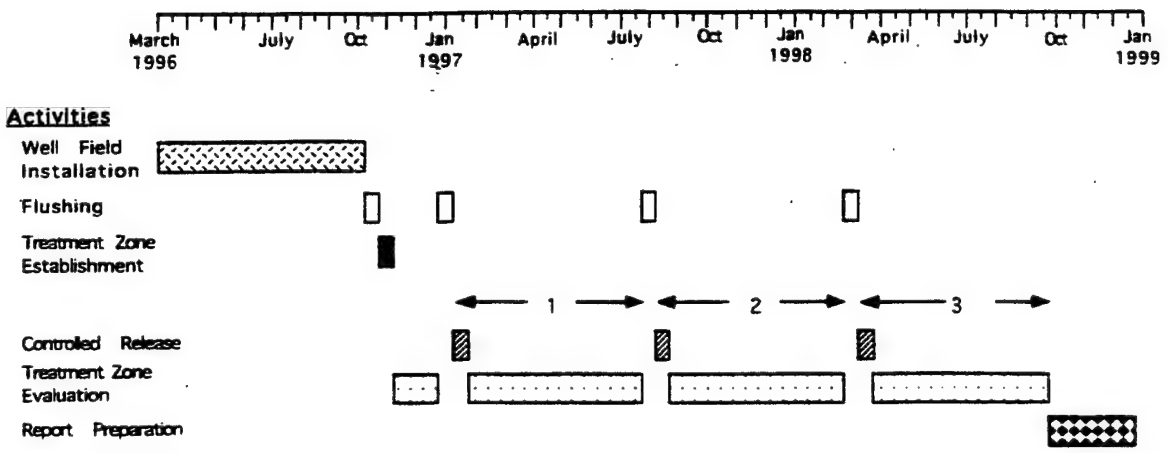

Figure 7. Time Line of Treatment Evaluations

Appendix C
Quality Assurance Project Plan

Modified June 1996

ESTCP

Technology Demonstration Plan

for

Enhanced In Situ Anaerobic Bioremediation of Fuel-Contaminated Ground Water

QUALITY ASSURANCE PROJECT PLAN

Prepared by:

GARY HOPKINS AND MARTIN REINHARD
DEPARTMENT OF CIVIL ENGINEERING
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305-4020

for:

NAVAL FACILITIES ENGINEERING SERVICE CENTER
CARMEN A. LEBRON
RESTORATION DEVELOPMENT BRANCH
1500 23RD AVE. ESC-411
PORT HUENEME, CA 93043

1.0 PROJECT ORGANIZATION

The technology demonstration will be a joint effort between the Naval Facilities Engineering Service Center (NFESC) and Stanford University. The responsibilities of the participants have been described in Section I.D. in the work plan. Quality assurance and quality control questions should be referred to the principal investigator for resolution.

2.0 QUALITY ASSURANCE PROJECT PLAN

This document describes the quality assurance and quality control procedures to be used during the conduct of the flow-through demonstration/evaluation of in-situ bioremediation of BTEX contaminated groundwater contamination using alternative electron acceptors at Seal Beach Naval Weapons Station. Work to be conducted during the demonstration includes physical, chemical, and microbiological characterization of the demonstration site, as well as monitoring of groundwater quality during and at the conclusion of the demonstration.

The Stanford University, Department of Civil Engineering, Environmental Engineering and Science Program Quality Assurance Program Plan is referenced in this plan. This plan will henceforth be referred to as the Stanford Environmental Engineering and Science Program QAPP.

The three treatment zones to be evaluated will be approximately 20 meters away from the extraction well. Each treatment well will receive ground water augmented with a different electron acceptor composition and thus, produce three distinctively different environments for evaluation of in situ biodegradation of the BTEX contaminants. In addition, bromide added to the ground water to serve as a tracer of water movement so that the relative amount of cleaned ground water passing a monitoring point can be determined.

The primary parameters to be monitored are the BTEX compounds (benzene, toluene, ethylbenzene, and the xylene isomers), the electron acceptors (oxygen, nitrate, and sulfate), the tracer (bromide) and pH. Specific metabolites will be analyzed to for process verification.

This QA/QC plan foresees that an automated, on-line analytical system will be used. The automated system will measure all parameters except carbonate and metabolites. This system will be described in detail in the sections below.

2.1 QUALITY ASSURANCE OBJECTIVES

As discussed in the work plan, the objective of this project is to demonstrate and evaluate the efficacy of in-situ anaerobic bioremediation of BTEX within an existing BTEX contaminated field site using alternative electron acceptors. To help ensure that the aquifer system is well understood prior to operation of the demonstration system a series of laboratory, modeling, and preliminary field work has been performed. Using cores obtained from the aquifer, microbiological studies have been conducted in the laboratory to evaluate the microbiological characteristics of the aquifer. These studies have demonstrated degradation of the primary substrates, BTEX, can be expected in the field. Similarly, laboratory sorption studies will be accomplished to evaluate the sorptive characteristics of the aquifer solids using core material obtained previously as well as core materials to be retrieved during the installation of the treatment wells. The physical, chemical, and biological parameters obtained from these analyses will be used to develop a simulation model for the site as an aid in design and operation of an in-situ treatment system and to make subsequent evaluations of treatment effectiveness. During operation of the treatment system, an extensive number of samples are required over time and space, with nearly real-time analysis. These extensive data are needed so that system efficacy can be evaluated over time, and system modifications can be made during operation if necessary. In addition, as the treatment system involves injecting alternative electron acceptors into the ground water, extensive near real-time monitoring is required to ensure control over the fate of the injected chemicals.

2.1.1 DATA QUALITY OBJECTIVES

The purpose of defining data quality objectives (DQO) is to ensure the data obtained is scientifically sound and useful in the evaluation of the biodegradation demonstration. The physical process of collecting samples, shipping and handling prior to analysis, instrument calibration procedures and sample preparation affect the quality of the data results. The automation of these processes for the primary parameters (BTEX, electron acceptors, tracer, etc.) eliminates the human handling errors associated with sample collection and processing. The DQO for automated analytical systems is therefore focused on the instrument calibrations and representativeness of the samples collected to the in situ environment.

The commonly used criteria for DQOs are: 1) accuracy: the degree of agreement between measurements and the actual or true values of the sample, 2) precision: the degree of mutual agreement among a number of individual measurements, 3) completeness: the amount of

validated or useful data relative to the number of sample parameters collected, 4) representativeness: the degree to which the measurement accurately and precisely represents the parameter for the condition or operation, and 4) comparability: defines the confidence for comparing one data set to another and requires the samples to be representative with known precision and accuracy.

Accuracy

Accuracy, the degree of agreement between measurements and the actual or true values of the sample, is commonly determined by analysis of spike recoveries, generally surrogate and quality control checks (QCC). Surrogate spike compounds are normally analytes not found within the sample matrix but added to each individual sample for the data validation of accuracy. QCC are spiked samples prepared from commercially available stock solutions having at least five target analytes and are generally used to evaluate loss of instrument sensitivity and are thus of low concentration. Accuracy as measured by spike recovery is expressed as percent recovery (%R):

$$\%R = C_M / C_S \text{ X } 100$$

where C_M = measured concentration of analyte and C_S = spike concentration of analyte. For the samples collected by the automated sampling and analysis platform, it is not possible to add surrogate spikes to the samples, thus only QCC samples, at two concentration levels, will be analyzed daily in the off-line mode. For laboratory samples, surrogate spikes will be added to samples and % Recovery tabulated for all ground water samples. Laboratory QCC samples will also be used whenever appropriate standards are commercially available, otherwise, in-house QCC sample will be produced.

Precision

Precision, the degree of mutual agreement among a number of individual measurements, is commonly determined by analysis of duplicate and replicate samples. Duplicate samples are collected in a common container and then transferred to two or more individual containers while replicate samples are collected sequentially in individual containers. Precision can be expressed as percent relative difference (% RD):

$$\% \text{ RD} = (C_1 - C_2) / ((C_1 + C_2)/2) \text{ X } 100$$

where C_1 and C_2 are the individual measurements for the duplicate or replicate samples.

When large data sets are collected from and system which is in "steady-state," precision can also be evaluated by the percent relative standard deviation (% RSD):

$$\% \text{ RSD} = (\sigma/\mu) \text{ X } 100$$

where σ = standard deviation and μ = mean value. For the samples collected by the automated sampling and analysis platform, it is not possible to produce a duplicate sample but there are two forms of replicate sample analysis. The automated system has a replicate VOA sampler installed which automatically collects assigned replicate sample which can be analyzed later in the off-line mode. In addition, the sample location can be resampled immediately after analysis, with or without sample line flushing, to produce a replicate analysis (assumes near steady-state conditions exist). Both forms of replicate analysis will be incorporated with the resampling of one or more sample locations being performed daily. The analysis of precision based upon % RSD will be watched, but until steady-state conditions are known to exist, will be considered secondary. For laboratory samples, either duplicate or replicate samples will be analyzed at a rate of 10%, selection of type will depend upon sampling procedures.

Completeness

Completeness, the amount of validated or useful data relative to the number of sample parameters collected, would ideally be 100%. Percent completeness (%C) can be expresses as:

$$\%C = \text{Number of Data Points} / (\text{Sample Count X Parameters}) \text{ X } 100$$

For the samples collected by the automated sampling and analysis platform, it is not possible obtain this value since all instruments eventually have some form of problems and operators are not always on site. Problems encountered may result from mechanical failure, electrical failures or operator errors although may of the problems may be avoided by following standard operating procedures (SOP) and preventative maintenance. The automated system is expected to process approximately 40 samples per day, each producing at least 12 data point, or a total of 480 data point per day. Thus, for a two year demonstration, approximately 350,000 individual data points would be collected if %C were 100%. A %C much lower should still provide sufficient data for this demonstration and therefore completeness is not considered important for field instrumentation. For the laboratory analysis, %C in access of 90% is expected as in past field projects.

Representativeness

Representativeness, the degree to which the measurement accurately and precisely represents the paramenter for the condition or operation, is not easily quantifiable. Within the subsurface environment, stratification of the aquifer solids (clay lenses embedded in sandy zones) can produce micro-environments which have entirely different redox potentials when compared to the bulk ground water surrounding them. The use on multi-level sampling points within a single borehole allows both the detection of these micro-environments and produces sufficient data for statistical analysis of the bulk ground water chemical concentrations. The use of automated on-line sampling and analysis minimizes potential changes in chemical composition and therefore should increase the representativeness of the resulting data.

For the field samples shipped to the laboratory, proper sample collection, shipping and storage are required to ensure representative results are obtained. For samples produced within the laboratory from bench scale experiments, sampling and analysis procedures will be reviewed regularly to ensure representativeness.

Comparability

Comparability, defines the confidence for comparing one data set to another and requires the samples to be representative with known precision and accuracy. Comparability for the automated sampling and analysis platform can be assessed by inter-laboratory comparison of the automated VOA replicate sample. It is anticipated that three replicate VOA samples per week will be shipped to the Stanford Water Quality Laboratory or to a commercial contract laboratory for analysis and comparison of the results to the data collected on-line. If the Water Quality Laboratory is used, then this also provides the comparability for the laboratory as well.

Representativeness has no specific DQO. Comparability also has no specific DQO but will be checked by inter-laboratory analysis. DQO for completeness for both samples shipped to the laboratory and the automated sampling and analysis platform is 90%. The accuracy and precision objectives that will be used in sampling for BTEX contaminants, inorganic anions (bromide, nitrate and sulfate), dissolved oxygen (DO) and pH are indicated in Table 2-1.

TABLE 2-1. ACCURACY AND PRECISION OBJECTIVES FOR GROUNDWATER SAMPLES

Parameter	Laboratory			Field		
	Method	Accuracy(a)	Precision (b)	Method	Accuracy	Precision
BTEX	EPA 502.2 GC/PID(d)	± 20%	20%	ASAP(c) GC/PID(d)	± 20%	20%
Anions	EPA 300.0	± 25%	15%	ASAP	± 15%	15%
DO	EPA 360.1	± 10%	5%	EPA 360.1	± 10%	5%
pH	EPA 403	± 10%	5%	EPA 403	± 10%	5%

(a) Total error for a single measurement, including both systematic error (bias) and random error (variability due to imprecision), expressed as a percentage of the measured value.

(b) Relative percent difference for replicate determinations (including sample variability).

(c) Automated sampling and analysis platform (A+RT Inc). See the Superfund Innovative Technology Evaluation (SITE) report titled *Automated On-Site Measurement of Volatile Organic Compounds in Water: A Demonstration of the A+RT, Inc. Volatile Organic Analysis System*, EPA Report EPA/600/R-93/109, June 1993 for a discussion of the ASAP system performance.

(d) Gas Chromatograph/Photoionization Detector

2.1.2 DETECTION LIMIT OBJECTIVES

For data validation, a statistical analysis of practical detection limits and practical quantitation limits will be performed after the automated sampling and analysis platform is installed and operational, but before full system operations begin. For the volatile compounds, BTEX, detection limits on the order of 1 µg/L are anticipated. A detection limit of 1 µg/L for benzene should be sufficient since the EPA maximum contaminant level in drinking water is 5 µg/L, and the California drinking water maximum level recommendation for toluene is 18 µg/L. Therefore, benzene at concentrations below the detection limit in the reinjected ground water will have no adverse impact on water quality. The other BTEX compound have much higher MCLs than benzene. Also, since the anticipated initial ground

water concentrations for the BTEX compounds are expected to be in the mg/L range, a detection limit of 1 µg/L is more than sufficient to monitor bioremediation performance.

The concentration of bromide added to the groundwater to help evaluate the zone of impact of the demonstration was set based upon the attainable detection limit for bromide. As a detection limit of 0.5 mg/L has been found to be attainable in past field experiments, bromide will be added to the groundwater at 50 mg/L, so that the detection limit is 1% of the added bromide concentration.

The measurement of DO during the demonstration is to ensure anaerobic conditions are maintained in the groundwater. Thus, a detection limit for DO of 0.2 mg/L is adequate to determine whether or not the system is anaerobic since oxygen concentrations below the detection limit would be readily consumed.

2.2 FIELD SAMPLING PROCEDURES

2.2.1 MONITORING WELL LOCATIONS

A series of 15 monitoring wells will be installed around and within the demonstration treatment zone. The wells will be composed of seven 3/16" stainless steel tubes spaced 14" apart, thus creating a sample bundle where each tube will reach to a different depth in the aquifer. Each of the three treatment zones will have 5 multilevel sample bundles associated with it. For each zone, one multilevel sample well will be located approximately 7 meters upgradient of the injection well and two multilevel sample wells well be located two and four meters in the direction of the extraction well. For two of the treatment zones, an additional two multilevel sample wells will be located approximately in the direction of the natural gradient, two and four meters from the injection well. For the treatment zone upgradient from the extraction well, the two remaining multilevel sample wells will be placed 6 and 8 meters downgradient continuing the line in the direction of the extraction well.

2.2.2 SAMPLING PROTOCOLS

2.2.2.1 Drilling. Drilling of the three injection wells and the extraction well will be accomplished by using a sonic rig when soil borings are required. The monitoring wells may also be installed using a sonic drill rig, but other techniques are currently being investigated.

2.2.2.2 Soil Sampling. Soil samples will be collected whenever possible. In past drilling campaigns, soil samples have been collected using a California split-spoon samples. It is unknown if the sonic drill rig is able to use the split-spoon sampler, or if longer continuous core barrels will be used. If using the split-spoon sampling technique, the method will follow the American Society for Testing Materials (ASTM) "Standard Methods for Penetration Test and Split Sampling of Soils" (ASTM D1586). However, the penetration test will not be performed, and the sampling barrel will have an outer diameter of 2 inches. For samples being obtained for microbiological analysis, the sampling barrel will have been wrapped in paper and autoclaved prior to use. Standard identification techniques (ASTM D2488) will be followed and samples will be described using the Unified Soil Classification System. In addition, the ends of the core barrels will be photographed prior to sealing.

2.2.2.3 Well installation. Well installation will include well construction, well head completion, and well development. The injection wells and the extraction well will be constructed of stainless steel wire wound screens with schedule 40 PVC risers. The injection wells will be 2" inside diameter and installed in a 8" diameter borehole. The extraction wells will be 6" inside diameter and installed in a 11.5" diameter borehole. The well screens will be 7 feet long and the slot size will be 0.010". The sand pack around the screens will be Lone Star #2/16 sand and this sand pack will extend at least one foot above the screen. At least one foot of transition sand, Lone Star #1/20, will be added before the bentonite seal is placed. The bentonite seal will be composed of at least two feet of 1/4" pellets and hydrated with water for at least one hour before the grout stem to the surface is placed.

The monitoring wells are multi-level sampling devices composed of seven 3/16" stainless steel tubes with glass wool filters on the inlets. The construction of these monitoring wells will begin with hand augaring a 6" hole to roughly 6'. A 2" casing is driven to the final depth and the core material collected. The sample bundles are then placed in this 2" borehole. Lone Star #2/16 sand is used as a sand pack as the casing is removed from the borehole. For an annular seal, a 2" PVC well casing is placed around the sample bundle and 2 feet of bentonite pellets is then placed within the hand augared hole. Finally the remainder of the hole is filled with grout.

2.2.2.4 Automated groundwater sampling. The Automated Sampling and Analysis Platform (ASAP) will provide on-line analyses for up to 111 sample points collected automatically from the monitoring wells and injection flow streams. The connections between the ASAP system and the monitoring wells will be stainless steel tubing. After flushing the

sample lines, the ASAP extracts a sample and prepares separate aliquots for volatile organic analysis (VOA) using a modified purge and trap method for gas chromatography (for BTEX compounds), HPLC anion chromatography (for bromide and the electron acceptors), or specific ion probe analysis (for DO and pH). The ASAP system is designed to provide samples directly to the instrumentation without operator intervention and will be continuously operated 24 hours per day. The system also has a replicate VOA sample collector which can be programmed to collect replicate samples from any specific sample location or from all sample locations, for use in confirmatory analyses at other laboratories. Note however, the replicate sample must be manually removed before the next assigned replicate sample or else the replicate sample will be flushed and a new replicate will then begin to be collected.

2.2.2.5 Manual groundwater sampling. Samples will be collected manually from the monitoring wells which are not connected to the ASAP. These will be collected using the sampling manifold previously used for the slug test demonstrations. This manifold is designed to provide head space free sampling from six sample points simultaneously, filling standard 40 ml VOA bottles. The bottles, previously labeled, are then capped and placed on the ASAP for off-line automated analysis.

2.2.3. SAMPLE HANDLING FOR LABORATORY ANALYSIS

Samples for laboratory analysis will comply with the EPA-recommended container types and preservation methods (with HCl added to reduce the pH to 2 or lower. Sample containers will have been cleaned in accordance with EPA protocol. As each sample is collected in the field, it will be placed in a labeled sample container. The sample label will contain sufficient information to identify the unique sample in the absence of other documentation (sample I.D. number, well number, date, sampling depth). The sample label will be affixed directly to the sample container and will be completed in indelible ink.

Soil samples collected by the split-spoon technique will consist of brass core barrels sealed with plastic caps. As noted in section 2.2.1.2, core barrels used for microbiological analyses will have been autoclaved and paper-wrapped prior to use. Upon removal of the core barrels from the split-spoon sampler, they will be photographed with the collection depth noted. The barrels will then be capped with the well number and depth written on the cap, and placed in an ice chest.

Sample collection logs will be completed in the field for each sample collected. Figure 2-1 is an example of the groundwater sampling log form to be used.

Samples which are to be analyzed in the Stanford Water Quality Laboratory may be hand-carried back to Stanford so long as the holding time to analysis will not exceed two weeks and sample are maintained at low temperatures. Otherwise, samples will be prepared for shipment by packing in coolers with inert cushioning material. The samples will then be shipped to either a commercial laboratory or Stanford, as required. Shipments to Stanford will be sent to the following address, using an appropriate carrier such as UPS or FEDEX, and according to Department of Transportation regulations:

Name of Researcher Responsible for Analysis
Department of Civil Engineering
Terman Engineering Center
MC: 4020
Stanford University
Stanford, CA 94305-5020

Phone: 415-723-8574/4123

Upon arrival of the samples at the laboratory, the researcher responsible for analysis will note the arrival date/time in his or her laboratory notebook and the Master Seal Beach Sample Log Notebook which will be kept in Room B53, Terman Engineering Center.

GROUNDWATER SAMPLING LOG

Project Name Seal Beach NWS Bioremediation Demonstration

Well Number _____ Recorded By

_____

Sample Number _____ Date

_____

Duplicate Number _____

Sampling Information

Analytical Parameter	Sampling Depth	✔ If Field Filtered	Preservation Method	Volume Required	Sample Bottle I.D.s

Figure 2-1.

For samples being used for regulatory purposes chain-of-custody procedures will be followed and samples will be shipped to an analytical laboratory approved by the California Department of Health Services. Chain of custody forms will be kept in the Master Seal Beach Sample Log Notebook in Room B53, Terman Engineering Center .

2.2.4 CALIBRATION PROCEDURES AND FREQUENCIES FOR FIELD TEST EQUIPMENT

It is anticipated that the following equipment will be used in the field to gather data:

- pH probe with Temperature Output
- DO probe with Temperature Output
- Automated sampling and analysis platform (ASAP)

All calibrations will follow manufactures specification.

One of the features incorporated in the ASAP is automated off-line sample analysis which may be used for automated analysis of continuing calibration checks (CCC) and calibration samples. The ASAP computer system recognizes designated sample names beginning with "CCC" as CCC samples, sample names beginning with "CAL" as calibration samples, sample names beginning with "QCC" as quality control check samples and sample names beginning with "BLANK" as blank samples. These samples are treated differently by the central computer when the resulting data is returned for storage in the database. The CCC samples, QCC samples and BLANK samples are stored in a QA/QC database, which is separate from the sample database. The results of the CCC samples are used to determine the need for recalibration.

Variable parameters can be selected to automate calibration based upon the CCC results. For example, any one of the analytes found to be different than the expected "true" value by 25% or more can initiate a calibration sequence, or, if the average difference is in excess of 15% a calibration sequence can be initiated. Also, since each chromatographic detector can be expected to have a different variability, other "difference" values can be assigned to the parameters for each type of analysis (GC/PID, GC/ELCD, GC/FID or HPLC Conductivity). Such difference values will be selected based upon the accuracy and precision values presented in Table 2-1 and the initial testing of the system when installed. Although not the normal practice, the CCC sample will be used as the calibration sample for the ion chromatograph and the calibration sample for the GCs. CCC samples will be processed at least twice a day and thus are expected to represent about 5% of the analyses. Similarly,

automated QCC (at two concentration levels) and Blank samples will also be run at least twice a day. Thus, 15% of the samples analyzed will be used for QA/QC purposes.

Upon an automated calibration run, the integrators are set to calibrate at the end of the calibration run, i.e. calculate new response factors. The resulting response factors are then used for subsequent analyses. Also the new response factors are stored in a third database (the first two databases being the sample database, and the QA/QC database). Here the operator can review the results and over a period of time and can readily detect changes in the detector performance, which would be indicated by trends in the response factor values.

For the initial setup, multi-level calibrations of at least 5 points will be used to determine linearity of response by the detectors. Once known, the sample loop for GC analysis assigned to each sample location will ensure the analysis is in the linear range and above the Practical Quantitation Limit (or Reporting Limit). Thereafter, calibration will be single point and will assume a zero intercept if determined to be appropriate.

The probes cannot be calibrated automatically. Here the probes will be calibrated each day an operator is present, with the pH probe using a two point calibration (pH=7 and pH=4) and the DO probe a single point calibration using water at DO equilibrium with atmospheric air, and using temperature correction.

2.3 ANALYTICAL PROCEDURES

2.3.1 AUTOMATED SAMPLING AND ANALYSIS PLATFORM (ASAP)

The ASAP will process samples for analyses of BTEX along with other aromatic and aliphatic compounds by GC (modified Method 502.2); anions (bromide and the electron acceptors) will be analyzed by HPLC using anion chromatography with direct reading conductivity detector, and probes will be used for the measurement of DO and pH. The modifications of Method 502.2 will be: the use of the A+RT Volatile Organic Analysis System (AVOAS) sample preparation instead of a conventional purge and trap concentrator, capillary column instead of a packed column and the use of either a PID/FID in series or a pulsed discharge helium ionization detector (PDHID). The analyte list will also be decreased to target the known contaminants at this location. The method detection limits for the ASAP for the parameters of interest are as follows

BTEX	1 µg/L
DO	0.1 mg/L
Anions	0.5 mg/L

The A+RT Volatile Organic Analysis System (AVOAS) uses a sample loop to provide a specific and reproducible sample volume, which is then He stripped of the volatile hydrocarbons, which are then trapped on standard sorbent traps. The volatile hydrocarbons are then thermally desorbed into the GC carrier flow for subsequent chromatographic separation and detection by appropriate detectors. The overall method is very similar to conventional "purge and trap" but is more rugged and self cleaning. In addition, a multi-position sample loop valve is used to expand the range of analysis by approximately two order of magnitude; thus for most GC detectors, the AVOAS has a dynamic range of 5 orders of magnitude (for ELCD, about 10 ng/L to 5 mg/L). This system was successfully evaluated under the Superfund Innovative Technology Evaluation (SITE) program (EPA/600/R-93/109) . The AVOAS was found to produce results similar to the results of the evaluation laboratory which analyzed the duplicate samples using Method 502.2. The AVOAS was found to have slightly lower precision (results more variable) but greater accuracy (closer to spiked "true" concentrations). Overall, the AVOAS will be able to meet the DQO presented in Table 2-1.

The gas chromatograph used in the automated system will incorporate a tandem PID/FID or PDHID. The capillary column to be used is a J&W Scientific 30 meter megabore DB-WAX column.

The inorganic anions, bromide and the electron acceptors, will be measured by direct reading ion chromatography. Here, a Wescan conductivity detector is connected to a standard anion HPLC column (Alltech Associates) and 0.04 mM Potassium Biphthalate (KHP) is used as an eluant. Using a 100 µL sample loop, this system provides a 0.5 to 100 mg/L bromide linear range.

For DO and pH, standard probes and meters are used. Here the ASAP system flushes electronically isolated flow through cells and the resulting probe/meter measurements are stored in the data base.

Daily standard maintenance of the ASAP requires back-flushing of the stainless steel sample filters, checking (and changing as needed) compressed gases and integrator paper and pens, refilling the KHP stock solution for the ion chromatograph, and calibration of DO and pH probes. Although the SOP requires these things daily, they will be performed on Mondays, Wednesdays and Fridays since this field location is remote to the operators. Should this be found insufficient, a new schedule will be arranged. The weekly standard maintenance includes changes of pump tubes. All of these maintenance procedures can be accomplished without shutting down the analytical system. As needed, guard columns and analytical columns for the ion chromatograph may require replacement. This will require a system shut down of approximately 45 minutes.

2.3.2 OTHER FIELD ANALYSES

Other field anaylses may include the use of test strips for the presence of soluble sulfide and spectrophotometric measurement of ferric ion producing semi-qunatitative results. Both methods were used during the slug test demonstrations and the results indicated no significant quantities present, i.e. results at or below detection limits. Thus, although these analyses will continue and results entered into the database when taken, they will only be obtained irregularly.

2.3.3 LABORATORY ANALYSES

Laboratory analyses, as required for specific parameters of interest (e.g. hardness, alkalinity, total dissolved solids, metals, etc.), will be accomplished by either the Stanford Department of Civil Engineering Laboratory or a California Department of Health Services approved laboratory in accordance with the procedures specified in the Stanford Environmental Engineering and Science Program QAPP.

2.4 DATA MANAGEMENT, REDUCTION, AND REPORTING

2.4.1 AUTOMATED SAMPLING AND ANALYSIS PLATFORM (ASAP)

Data obtained from the ASAP is stored automatically in a sample database on the central computer and is organized chronologically. Hard copies of the GC and HPLC chromatograms and resulting data are produced automatically on the integrators and used to validate the stored data. If the data is found to be invalid due to integrator problems (response time errors or integration parameter problems) the chromatogram can be reprocessed and corrected through the A+RT software if done before the chromatogram is erased (chromatograms are saved for approximately 1 day). After which, any changes made to the data base would have to be done manually. The database can be accessed remotely via another computer and modem through the A+RT software, but manual changes to the database cannot be made via the remote connection.

The ASAP computer (different than the central computer) is responsible for the selection of sample locations and processing of the samples, both on-line and off-line. During the processing of the AVOAS samples, there are a number of error checking routines that are used to evaluate the validity of the individual samples. At the beginning of the chromatograph runs, the sample location, time stamp of the sample collection, sample loop used for GC and sample preparation error code are transferred to the central computer and added to the database. The same information is transferred to the integrators and is appended to the hard copy of the chromatograph. This information is thus readily available to the responsible operator when the data is validated daily.

Data is not generally rejected from the data base unless there is confirmed problem with the instrumentation, such as a plugged sample loop or fitting. When this happens, it usually results in the loss of several hours worth of data. It should be noted that a loss of data from one portion of the instrument system does not usually coincide with loss in another portion of the system. Data points are never rejected from the database even if they are statistically outliers, although they may be deleted from the normal graphic plots used in reports.

2.4.2 OTHER LABORATORY AND FIELD ANALYSES

Raw data and processed data will be recorded in bound laboratory notebooks. Computer printouts may be kept in binding folders designed for that purpose, provided that the data are

cross referenced to the laboratory notebook. Where possible, electronic records will be kept on separate diskettes identified and cross referenced in the laboratory notebook. Each sample and analysis should be uniquely identified so that samples can be tracked unambiguously. Computerized data entry operations will be manually verified for accuracy. Computer backups will be used. All records described above will be maintained for a period of not less than five years following termination of the project.

2.4.3 DATA REPORTING

Reports will be made in two ways: (1) as annual reports to the Training and Technology Transfer Advisory Committee (TTTAC) of the Western Region Hazardous Substance Research Center (WRHSRC); and (2) as publications in peer reviewed scientific journals. Annual reports will contain a summary of progress and the important results up to that date. The final report will contain a complete analysis of results and discussion of the findings. Reports will contain specific QA/QC information that is needed to establish the reliability of the research. Specific QA/QC reports will not be made.

2.5 QUALITY ASSURANCE/QUALITY CONTROL CHECKS

2.5.1 AUTOMATED SAMPLING AND ANALYSIS PLATFORM (ASAP)

The collection of duplicate samples is not possible using the ASAP on-line system since a duplicate implies the splitting of a single sample into two separate but equal subsamples. It is possible to manually collect duplicate samples and analyze them in the off-line mode. Since there will be manually collected samples from wells not connected to the ASAP, some of these samples can be collected in duplicate and used for evaluation as such as well as for interlaboratory comparison.

The automated analysis of "near" replicate samples is possible in either of two ways. One method involves the automated collection of the sample in a standard 40 mL VOA bottle which can then be used as a replicate and analyzed in the off-line mode (or the replicate can be shipped to another lab for analysis for interlab comparison). Another method is to assign a second sample name to a sample location, use the same (or different) sample loop and assign a zero flush time for the sample line. In this method the replicate sample is held in the stainless steel sample line until being processed on-line. The second of these methods is slightly better in that there is no need for operator intervention and the sample is not exposed to air during the capping of the 40 mL sample bottle. The second method will be used and

three sample locations will be selected for this comparison throughout the demonstration, thus approximately 4% of total sample throughput will be dedicated to replicate analysis.

Spiked samples are generally used for the evaluation of analytical laboratory accuracy. Since our main concern is the relative change in concentration during the demonstration and not necessarily absolute concentrations, spiked samples will not be analyzed during this demonstration. QCC samples will be used instead.

One of the limitations of the AVOAS identified in the SITE report was the inability to add surrogate spikes to the samples processed in the on-line mode. The ASAP-AVOAS to be used at the Seal Beach NWS field site does not have the surrogate spike module and thus surrogate spiking of the on-line sample is not possible.

Blank samples will be analyzed approximately twice per day. The main goal of the blank samples will be to determine if there is sample carryover in the sample loops. Thus, the location of the blanks within the sample order sequence will be varied on a regular basis, as will the sample loop used for the analysis.

The ASAP uses automated continuing calibration checks (CCC) and blank samples to ensure the consistency of the data produced by the system (see section 2.2.2). The use of the CCC samples to initiate a calibration run, or recalculation as a calibration sample, should ensure the calibration does not drift significantly if CCC samples are processed twice per day. The separate storage of these results in a QA/QC database along with a similar number of blank samples facilitates the development of QA/QC reports and the validation of the field samples. The storage of the individual calibration response factors in the response factor database further assists in the maintenance of the analytical system and can be used in QA/QC analysis for the individual detectors. The storage of the AVOAS error codes associated with each individual field sample in the database can be used to evaluate general performance of the system and individual sample loops.

Overall, 15% to 20% of the sample throughput will be dedicated to QA/QC samples.

2.5.2 STANFORD LABORATORY ANALYSES

Stanford laboratory analyses will be conducted in accordance with the Stanford Environmental Engineering and Science Program QAPP.

2.5.3 CALIFORNIA DEPARTMENT OF HEALTH SERVICES APPROVED LABORATORY ANALYSES

Samples processed by California Department of Health Services certified laboratories will include surrogate spiking of samples and report of surrogate recovery. EPA method 624 will be used for the analysis of volatile organic compounds (including BTEX).

2.5.4 PROJECT QUALITY ASSURANCE (QA)

QA activities associated with this project include:

- Preparation and approval of this QAPP
- Replicate sample analysis by the ASAP, Stanford, and California DHS approved labs
- Oversight of project activities by the WRHSRC TTTAC
- Validation of the ASAP through the EPA Superfund Innovative Technology Evaluation (SITE) Program
- Peer review of results reported in journal papers

2.6 CORRECTIVE ACTIONS

Changes which potentially result in a modified or a new SOP will be evaluated with duplicate samples and standards and compared to existing SOP prior to being implemented on active samples. Such changes will not be implemented until approval is received from principle investigator or quality control officer and will be documented by the respective signature on the new or modified SOP. Documentation is to be maintained in the Master QA/QC binder stored in Terman B-53.

2.7 QUALITY ASSURANCE REPORTS

As noted in section 2.4.3 above, progress reports will contain QA/QC information that is needed to establish the reliability of the research. However, specific QA/QC reports will not be prepared.

Appendix D
Well Logs

Project:	Stanford Univ. Bioremedation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	15 Feet	**SU43-1**
		Date:	14 June 1996	
Drilling Co.:	Water Development Inc.	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Resonant Sonic/4.5" Pipe	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SM		Moderate yellowish brown (10YR 5/4), moist in upper 1", dry to 1.75',silty, fine to coarse SAND
		17		CL		Moderate brown (5YR 3/4), dry to slightly damp, silty, CLAY; slight hydrocarbon odor
		5		SM		Dark yellowish brown (10YR 5/4),moist, silty, medium to coarse SAND
		801		SP		Medium blueish gray (5B 5/1), moist to saturated, coarse SAND, with some gravel up to 1/2 inch in diameter; strong hydrocarbon odor; water level measured at 7'2"
		41		ML		Dark greenish gray (5GY 4/1), damp, SILT; hydrocarbon odor
10		2		SM		Mottled moderate brown (5Y 4/4) and dark greenish gray (5GY 4/1), saturated, silty, fine SAND
		2		SP		Moderate brown (5Y 4/4), moist, fine to medium SAND; no odor
				CL		Dark yellowish brown (10YR 4/2), moist, silty, CLAY from 14 to 14.5 feet below grade
				SP		Moderate yellowish brown (10YR 4/2), moist, medium SAND from 14.5 to 15 feet below grade
						TOTAL DEPTH = 15 FEET
20						
30						

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Joshua Ong, Ph.D.
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Project:	Stanford Univ. Bioremedation Field Site	Project No.: OC 826G3.287	BORING NO.: SU43-2
Site Address:	Seal Beach Naval Weapons Station Seal Beach, California	Total Depth: 16 Feet Date: 14 June 1996	
Drilling Co.:	Water Development Inc.	Logged by: Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Resonant Sonic/4.5" Pipe	Reviewed by: Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		0		ML		Moderate brown (5YR 4/4), dry, sandy, SILT; no odor
				SM		Grayish orange (10YR 7/4), dry, silty, fine SAND from 2.5 to 3 feet below grade
		0		CL		Dark yellowish brown (10YR 4/2), dry, CLAY
						damp, sandy
						moist
		1,412		SP		Medium gray (N5), saturated, coarse SAND; strong hydrocarbon odor
		366		CL		Medium gray (N5), moist, CLAY
10		390		ML		Mottled medium gray (N5) and moderate brown (5YR 4/4), moist, SILT; moderate hydrocarbon odor
		117		SM/ML		Moderate reddish brown (10R 4/6), damp, silty, fine SAND to fine sandy, SILT
				CL		Mottled light brown (5YR 5/6), and pale yellowish brown (10YR 6/2), damp, CLAY
				SP		Moderate brown (5YR 4/4), moist, medium SAND; no odor
		0				TOTAL DEPTH = 16 FEET
20						
30						
40						

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Joshua Ong, Ph.D.
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.: SU43-2-B1
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16 Feet	
		Date:	26 June 1996	
Drilling Co.:	Precision	Logged by:	Scott Traub	Page 1 of 1
Rig/Auger Type:	Cushman with Jack Hammer/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		7.6	NA	CL		Olive black (5Y 2/1), damp, fine sandy, silty, **CLAY**; hydrocarbon/organic odor dark greenish gray (5GY 4/1)
				SM		Dark yellowish brown (10YR 4/2), damp, silty, fine SAND
		0	NA			very moist; slight hydrocarbon odor
				SP		Grayish olive (10Y 4/2), saturated, fine SAND; hydrocarbon odor
				SW		fine to coarse SAND
10		10	NA	SM		Olive gray (5Y 3/2), very moist, silty, fine SAND grayish olive (10Y 4/2)
		2	NA			dusky yellowish green (10GY 3/2); slight hydrocarbon odor
		30	NA	SP		Moderate yellowish brown (10YR 4/2), saturated, fine to medium SAND; no odor
		0	NA			
						TOTAL DEPTH = 16 FEET
20						
30						
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.: SU43-2-B2
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16 Feet	
		Date:	26 June 1996	
Drilling Co.:	Precision	Logged by:	Scott Traub	Page 1 of 1
Rig/Auger Type:	Cushman with Jack Hammer/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SC		Grayish olive green (5GY 3/2), damp, clayey, fine SAND; no odor
		0	NA	SM		Grayish olive green (5GY 3/2), very moist, silty, fine SAND; slight hydrocarbon odor
						saturated
10		523	NA	SW		Grayish olive green (5GY 3/2), saturated, fine to coarse SAND; strong hydrocarbon odor
				SM		Grayish olive green (5GY 3/2), saturated, silty, fine SAND
		4	NA	SC		Dusky yellow green (5GY 5/2), saturated, clayey, silty, fine SAND; slight hydrocarbon odor
				ML		Moderate yellowish brown (10YR 5/4), saturated, fine sandy, SILT
				SP		Moderate brown (5YR 4/4), saturated, fine to medium SAND; very slight hydrocarbon odor
						TOTAL DEPTH = 16 FEET
20						
30						
40						

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Joshua Ong, Ph.D.
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	15.5 Feet	SU43-2-B3
		Date:	25 June 1996	
Drilling Co.:	Precision	Logged by:	Scott Traub	Page 1 of 1
Rig/Auger Type:	Cart Mounted/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SP		Moderate brown (5YR 4/4), slightly damp, fine to medium **SAND**
		NA	NA	CL		Light olive gray (5Y 5/2), damp, fine sandy, **CLAY**; slight hydrocarbon odor
		0	NA	SM		Dark yellowish brown (10YR 4/2), very moist, silty, fine **SAND** light olive gray (5Y 5/2), saturated; no odor
				ML		Olive gray (5Y 3/2), saturated, clayey, **SILT**
10		5	NA	SM		Grayish brown (5YR 3/2) mottled with light brown (5YR 6/4), very moist, silty, fine **SAND**; slight hydrocarbon odor
				ML		Dark yellowish brown (10YR 4/2), saturated, fine sandy, **SILT**; no odor
				SM		Moderate brown (5YR 3/4), saturated, silty, fine **SAND**
		0	NA	ML		Dark yellowish brown (10YR 4/2), saturated, fine sandy, **SILT**
				SP		Moderate brown (5YR 3/4), moist, fine to medium **SAND** moderate brown (5YR 4/4), saturated
						TOTAL DEPTH = 15.5 FEET
20						
30						
40						

REGISTERED GEOLOGIST
Joshua [illegible], Ph.D.
[illegible] 4723
Expires 03/98
STATE OF CALIFORNIA

Joshua Ong

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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16 Feet	SU43-2-B4
		Date:	25 June 1996	
Drilling Co.:	Precision	Logged by:	Scott Traub	Page 1 of 1
Rig/Auger Type:	Cart Mounted/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				ML		Dark yellowish brown (10YR 4/2), damp, clayey, fine to medium sandy, **SILT**
		5.0	NA			Olive gray (5Y 3/2), damp, fine sandy, SILT; hydrocarbon odor
		991	NA			very moist
		1,089		SP		Olive gray (5Y 3/2), saturated, coarse **SAND**; strong hydrocarbon odor
						very moist, silty
10		56	NA	SM		Dark yellowish brown (10YR 4/2), very moist, silty, fine **SAND**; slight hydrocarbon odor
						moderate brown (5YR 4/4), saturated
						mottled black (N1) and light brownish gray (5YR 6/1); no odor
		0	NA			dark yellowish brown (10YR 4/2)
						fine to medium **SAND**
						silty, fine **SAND**
						TOTAL DEPTH = 16 FEET
20						
30						
40						

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Joshua Ong, Ph.D.
No. 4725
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16 Feet	SU43-2-B5
		Date:	28 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		0	NA	CL		Moderate brown (5YR 4/4), damp, CLAY
		2	NA	SP		Medium gray (N5), damp, medium SAND
		17	NA			hydrocarbon product visible in soil
				ML		Medium gray (N5), damp, clayey, SILT
10		61	NA			
		0	NA	SP		Light brown (5YR 5/6), moist, fine SAND
						saturated
		0	NA			
						TOTAL DEPTH = 16 FEET
20						
30						
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Project:	Stanford Univ. Bioremedation Field Site	Project No.:	OC 826G3.287	BORING NO.: **SU43-3**
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16 Feet	
		Date:	15 June 1996	
Drilling Co.:	Water Development Inc.	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Resonant Sonic/4.5" Pipe	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				ML		Light brown (5YR 5/6), dry, sandy, **SILT**, with sparse gravel up to 1 inch in diameter; rootlets common
				CL		Moderate brown (5YR 4/5), dry, silty, **CLAY**; no odor
						damp
		0		SC		Light brown (5YR 6/4), damp, clayey, fine to medium **SAND**
		0		CL		Moderate yellowish brown (10YR 5/4), damp, silty, **CLAY**
		25		SC		Olive gray (5YR 4/1), damp, clayey, fine **SAND**; hydrocarbon odor
10		7		CL		Olive gray (5YR 4/1), slightly damp, CLAY; hydrocarbon odor
				SP		Medium blueish gray (5B 5/1), saturated, coarse **SAND**; hydrocarbon odor
		846				
				CL		Olive gray (5YR 4/1), moist, **CLAY**
		2		SP		Light brown (5YR 5/6), saturated, fine to medium **SAND** clayey
						TOTAL DEPTH = 16 FEET
20						
30						
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Joshua Ong, Ph.D.
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	15 Feet	SU43-3-B1
		Date:	26 June 1996	
Drilling Co.:	Precision	Logged by:	Scott Traub	Page 1 of 1
Rig/Auger Type:	Cushman with Jack Hammer/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SM		Moderate brown (5YR 4/4), damp, clayey, silty, fine SAND hydrocarbon odor
		8	NA			olive gray (5Y 3/2)
				SW		Grayish olive (10Y4/2), saturated, fine to coarse SAND diesel odor; possible presence of "free product"
10		187	NA			
				SM		Moderate brown (5YR 4/4), saturated, clayey, silty, fine SAND
		0	NA	SP		Moderate brown (5YR 4/4), saturated, fine to medium SAND; no odor moderate yellowish brown (10YR 5/4); slight hydrocarbon odor
		0	NA			
						TOTAL DEPTH = 15 FEET
20						
30						
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	15 Feet	SU43-3-B2
		Date:	26 June 1996	
Drilling Co.:	Precision	Logged by:	Scott Traub	Page 1 of 1
Rig/Auger Type:	Difficult Access/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SM		Moderate brown (5YR 4/4), moist, clayey, silty, fine SAND
		0	NA	CL		Dark yellowish brown (10YR 4/2), damp, silty, CLAY; no odor
				SM		Moderate brown (5YR 3/4), damp, silty, fine SAND
10		15	NA			grayish olive (10Y 4/2), moist, clayey; hydrocarbon odor
		5	NA			
		0	NA			moderate brown (5YR 4/4), moist, silty, fine SAND; no odor
		0	NA	ML		Moderate yellowish brown (10YR 5/4), damp, fine sandy, SILT
						TOTAL DEPTH = 15 FEET
20						
30						
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Joshua Ong, Ph.D.
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.: SU43-3-B3
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	14.5 Feet	
		Date:	26 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Cushman with Jack Hammer/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		12	NA	CL		Olive gray (5Y 4/1), damp, **CLAY**; no odor
		554	NA	SM		Greenish gray (5GY 6/1), very moist, silty, medium to coarse **SAND**; hydrocarbon odor
10		5	NA	SP		Olive gray (5Y 4/1), moist, fine **SAND**; slight hydrocarbon odor
		10	NA			
		0	NA	SM		Dark yellowish brown (10YR 4/2), moist, silty, fine SAND saturated
						TOTAL DEPTH = 14.5 FEET
20						
30						
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Project:	Stanford Univ. Bioremediation Field Site	Project No.: OC 826G3.287	BORING NO.: SU43-3-B4
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth: 14.5 Feet	
		Date: 27 June 1996	
Drilling Co.:	Precision	Logged by: Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Cushman with Jack Hammer/2.5" Rod	Reviewed by: Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		146	NA	CL		Mottled light brown (5YR 5/6) and olive gray (5Y 4/1), damp, silty, CLAY; hydrocarbon odor
				SP		Olive gray (5Y 4/1), saturated, medium to coarse SAND; hydrocarbon odor
		1,112	NA			
10		28	NA			moderate brown (5YR 4/4), saturated, fine SAND; slight hydrocarbon odor
		0	NA	SM		Moderate brown (5YR 4/4), saturated, silty, fine SAND
		0	NA	SP		Moderate brown (5YR 4/4), saturated, fine SAND
						TOTAL DEPTH = 14.5 FEET
20						
30						
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16 Feet	SU43-3-B5
		Date:	28 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		2	NA	SP		Moderate yellowish brown (10YR 5/4), dry, silty, medium to coarse SAND; no odor
		2	NA			slightly damp, fine to medium SAND
10		246	NA			medium gray (N5), very moist, medium SAND; "free product" present in sample tubes from 7 feet to 9.5 feet
		130	NA			light brown (5YR 5/6), moist, fine SAND; "free product" present in sample tubes from 10 feet to 13 feet
				CL		Darkish yellow orange (10YR 6/6), damp, CLAY
		0	NA	ML		Light brown (5YR 5/6), damp, SILT
						TOTAL DEPTH = 16 FEET
20						
30						
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Project:	Stanford Univ. Bioremedation Field Site	Project No.:	OC 826G3.287	BORING NO.: **SU43-4**
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	17 Feet	
		Date:	15 June 1996	
Drilling Co.:	Water Development Inc.	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Resonant Sonic/4.5" Pipe	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SM		~4 inch thick asphalt pavement Light brown (5YR 5/6), dry, silty, fine to coarse SAND, with gravel up to 1/2 inch in diameter
				CL		Moderate brown (5YR 4/4), damp, sandy, CLAY; no odor
		0				
				SC		Light brown (5YR 5/6), slightly damp, clayey, medium SAND
		0				
		1,053		SP		Medium dark gray (N4), saturated, coarse SAND (hydrocarbon odor)
10		2		CL		Dark greenish gray (5G 4/1), damp, silty, CLAY; no odor
				ML		Brownish gray (5YR 4/1), moist, sandy, SILT
				SP		Light brown (5YR 5/6), moist, fine to medium SAND
		0				
		0				fine SAND
						TOTAL DEPTH = 17 FEET
20						
30						
40						

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Joshua Ong, Ph.D.
No. 4723
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16.5 Feet	SU43-4-B1
		Date:	28 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		0	NA	SP		Light brown (5YR 5/6), slightly damp, medium to coarse SAND; no odor
		48	NA			
		626	NA			medium gray (N5), very moist, medium SAND; hydrocarbon odor
10		504	NA			
		5	NA	CL		Light olive gray (5Y 5/1), slightly damp, CLAY "free product" present in sample tubes from 10 feet to 13 feet light brown (5YR 5/6)
		0	NA	ML		Light brown (5YR 5/6), slightly damp, SILT
						TOTAL DEPTH = 16.5 FEET
20						
30						
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Joshua Ong, Ph.D.
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16.5 Feet	SU43-4-B2
		Date:	27 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		74	NA	CL		Olive gray (5Y 4/1), damp, **CLAY**
		228	NA	SP		Olive gray (5Y 4/1), damp, fine **SAND**; hydrocarbon odor
		184	NA			saturated, medium **SAND**
10						Lost sampled material during recovery of sampler
		102	NA	SP		Dark greenish gray (5GY 4/1), saturated, coarse **SAND**; hydrocarbon odor
						medium **SAND**
		0	NA	ML		Dusky yellow (5Y 6/4), damp, SILT
						TOTAL DEPTH = 16.5 FEET
20						
30						
40						

REGISTERED GEOLOGIST
Joshua Ong, Ph.D.
No. 4725
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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16.5 Feet	SU43-4-B3
		Date:	27 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		41	NA	CL		Olive gray (5Y 4/1), damp, CLAY; slight hydrocarbon odor
		305	NA			silty
		938	NA	SP		Medium dark gray (N4), saturated, medium to coarse SAND; hydrocarbon odor
10		130	NA			
		2	NA	CL		Moderate yellowish brown (10YR 5/4), damp, CLAY; no odor
				ML		Moderate yellowish brown (10YR 5/4), saturated, SILT dry
						TOTAL DEPTH = 16.5 FEET
20						
30						
40						

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Joshua Ong, Ph.D.
No. 4725
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Project:	Stanford Univ. Bioremediation Field Site	Project No.: OC 826G3.287	BORING NO.: SU43-4-B4
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth: 15.5 Feet Date: 27 June 1996	
Drilling Co.:	Precision	Logged by: Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by: Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
		0	NA	ML		Olive gray (5Y 4/1), damp, sandy, SILT; no odor
		2	NA			dark greenish gray (5GY 4/1), SILT; hydrocarbon odor
		74	NA	SP		Dark greenish gray (5GY 4/1), saturated, coarse SAND
10		110	NA			hydrocarbon product visible in sampled material
		20	NA			moderate yellowish brown (10YR 5/4), moist, fine to medium SAND
		2	NA	ML		Moderate brown (5YR 4/4), moist, SILT
				SP		Moderate brown (5YR 4/4), saturated, fine SAND
						TOTAL DEPTH = 15.5 FEET
20						
30						
40						

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Joshua Ong, Ph.D.
No. 4725
Expires 03/98
STATE OF CALIFORNIA

Joshua Ong

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Project:	Stanford Univ. Bioremediation Field Site	Project No.:	OC 826G3.287	BORING NO.:
Site Address:	Seal Beach Naval Weapons Station Seal Beach, CA	Total Depth:	16.5 Feet	SU43-4-B5
		Date:	28 June 1996	
Drilling Co.:	Precision	Logged by:	Robert Loeffler	Page 1 of 1
Rig/Auger Type:	Direct Push/2.5" Rod	Reviewed by:	Joshua Ong	

Depth (feet)	Sample ID	OVA Reading (ppm)	Blow Counts (per 6")	USCS Class	Graphic Log	Lithologic Description
				SP		Light brown (5YR 5/6), slightly damp, medium SAND; no odor
		0	NA			pale yellowish brown (10YR 6/2), damp, fine SAND
10		0	NA			
		0	NA			very moist, medium SAND
				ML		Pale yellowish brown (10YR 6/2), moist, clayey, SILT
		0	NA	SP		Dark yellowish brown (10YR 4/2), saturated, fine SAND
						TOTAL DEPTH = 16.5 FEET
20						
30						
40						

REGISTERED GEOLOGIST
Joshua Ong, Ph.D.
No. 4725
Expires 03/98
STATE OF CALIFORNIA

Joshua Ong

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W:\LOGS\LBCH4B5.SAM 07/22/96 @ 10:28 AM